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PREDICTION OF FATE OF SELECTED PRIORITY POLLUTANTS CONSIDERING THEIR TRANSFORMATION PRODUCTS USING IN-SILICO METHODS

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PREDICTION OF FATE OF SELECTED PRIORITY POLLUTANTS CONSIDERING THEIR TRANSFORMATION PRODUCTS USING IN-SILICO METHODS

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ABSTRACT

PREDICTION OF FATE OF SELECTED PRIORITY POLLUTANTS CONSIDERING THEIR TRANSFORMATION PRODUCTS USING IN-SILICO METHODS

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As the number of chemicals used in commerce is continuously increasing, the task of evaluating the fate of chemicals along with their impacts on the environment becomes challenging. In this study, fourteen priority pollutants, namely, aclonifen, alachlor, atrazine, BDE-153, bifenox, chlorfenvinphos, chlorpyrifos, DEHP, dicofol, diuron, hexachlorobutadiene, pentachlorobenzene, trichloromethane, and trifluralin as well as p,p’-DDT as an impurity of dicofol, were selected among the 45 priority pollutants regulated by the European Union (EU). Selection of chemicals was made based on abundance of literature studies, availability of kinetic data, as well as compatibility with modeling tools. Then, experimentally verified degradation products of each selected chemical were found from the literature. A total of 45 transformation products (TPs) were compiled, with the aim of investigating their contribution to the persistence of the parent compound and their individual tendency to distribute into the environment. Selected chemicals were evaluated according to how they distribute into the environment depending on mode-of-entry. Additionally, the primary persistence (PP) of each parent compound was determined to understand the effect of PP on joint persistence (JP). In-silico or computational methods offer simple, affordable, and safe quantitative chemical evaluation with respect to chemical distribution, fate, and persistence by introducing, physicochemical properties, degradation half-lives, and emission amount. EPI Suite^{TM} v4.11, June 2017 was employed for chemical-specific physicochemical property estimation in this study, whenever experimental data was unavailable. An evaluative multimedia (MM) model, namely, the Equilibrium Criterion (EQC) model Level III was used to evaluate the persistency and environmental distribution of selected priority pollutants and their TPs.

PP is the ratio of the amount of parent compound at a steady-state to its initial emitted amount. Persistence evaluation could not be satisfactory if only persistence of a parent compound, namely, PP is considered. This is because parent compounds convert into their TPs. These TPs pose secondary persistence (SP), so PP and SP are added to obtain JP for a substance family. Ratio between JP and PP indicates the influence of TPs on persistence of a parent compound. As the number of TPs increases, JP will increase. In addition to the number of TPs, persistence of TPs, namely SP of TPs have a considerable effect on JP. For hexachlorobutadiene and aclonifen, presence of their TPs does not have a significant contribution to JP. That's why JP/PP for hexachlorobutadiene and aclonifen is 1.3 and 1.4, respectively. On the other hand, this ratio is 105 and 12 for trichloromethane and dicofol, respectively. These high ratios demonstrate a high contribution of TPs on the joint persistence for trichloromethane and dicofol families. Lastly, the input media to which chemical is introduced in other words mode-of-entry of chemicals as well as half-life in a dominant medium are shown to have the highest impact on all types of persistence (i.e. PP, SP, JP).

Keywords: In-silico, Integrated Fate Modeling, Physicochemical Estimation Tool, Priority Pollutants, Transformation Products

ÖZ

SEÇİLEN ÖNCELİKLİ KİRLETİCİLER VE TRANSFORMASYON ÜRÜNLERİNİN BİLGİSAYARLI METOTLARLA AKIBETLERİNİN TAHMİN EDİLMESİ

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Endüstride kullanılan kimyasalların sayısı gün geçtikçe artarken kimyasalların akıbetlerini ve beraberinde çevreye olan etkilerini belirleme işi gayret gerektirmektedir. Bu çalışmada Avrupa Birliği tarafından izlenen 45 öncelikli kirleticiden 14 tanesi, aklonifen, alaklor, atrazin, BDE-153, bifenoks, diuron, dikofol, hekzakloro-bütadien, DEHP, trifluralin, trikloro-metan, pentakloro-benzen, klorfenvinfos, klorpirifos, ve ek olarak dikofol içerisindeki saflığı bozan maddelerden p,p'-DDT seçilmiştir. Kimyasalların seçimi sırasında, yapılan çalışmaların sayısı ve çeşitliliği, kinetik verilerin varlığı ve kullanılan modellerle uyumu göz önüne alınmıştır. Her bir seçilen kimyasal için deneysel olarak kanıtlanmış degradasyon ürünleri literatür taramasıyla bulunmuştur. Toplamda 45 transformasyon ürünü, ana kimyasalların kalıcılığına olan katkılarını ve tek başlarına doğadaki yayılım eğilimlerini araştırmak için derlenmiştir. Seçilen kimyasalların çevredeki dağılımlarının emisyonun yapılan medyaya bağlı olarak nasıl değiştiği değerlendirilmiştir. Ek olarak birincil kalıcılığın (PP) bütüncül kalıcılığa (JP) etkisini belirlemek için her ana kimyasalın birincil kalıcılığı belirlenmiştir. In-silico, diğer bir deyişle bilgisayar bazlı metotlar, kimyasal dağılımını, akıbetini ve kalıcılığını, kimyasalın yarılanma ömrünü, fizikokimyasal özelliklerini, ve emisyon miktarlarını kullanarak basit, ucuz, ve güvenilir şekilde değerlendirme imkanı sunar. Bu çalışmada, deneysel veri olmaması durumunda EPI Suite programı, Haziran 2017, kimyasal spesifik fizikokimyasal özellik girdilerini belirlemek için kullanılmıştır. Çoklu medya akıbet ve taşınım modellerinden EQC model Seviye III seçilen öncelikli kirleticilerin ve bu kirleticilerin transformasyon ürünlerinin kalıcılığını ve çevredeki dağılımlarını değerlendirmek üzere kullanılmıştır.

PP, ana kimyasalın kararlı haldeki miktarının emisyon edilen miktarına oranıdır. Sadece ana kimyasalın kalıcılığı baz alındığı sürece kalıcılık değerlendirmesi yeterli olmayacaktır. Bunun nedeni ana kimyasallar transformasyon ürünlerine dönüşecektir. Bu transformasyon ürünleri ikincil kalıcılığa neden olurlar. Böylece birincil ve ikincil kalıcılık toplanarak kimyasal ailesine ait JP elde edilebilir. Transformasyon ürünlerinin sayısı arttıkça bütüncül kalıcılık artacaktır. Transformasyon ürünlerinin sayısına ek olarak, transformasyon ürünlerinin kalıcılığı, yani transformasyon ürünlerinin ikincil kalıcılığının bütüncül kalıcılık üzerine önemli derecede etkisi vardır. Hekzakloro-bütadien ve aklonifenin transformasyon ürünlerinin JP'ye önemli derecede bir etkileri bulunmamaktadır. Bu nedenle JP ile PP arasındaki oran hekzakloro-bütadien için 1.3 ve aklonifen için de 1.4 değeridir. Öte yandan, bu oran triklorometan için 105, dikofol için de 12 değerindedir. Bu yüksek oranlar triklorometan ve dikofol kimyasallarının transformasyon ürünlerinin ilgili ailenin bütüncül kalıcılığı üzerindeki önemli etkilerini gösterir. Son olarak, kimyasalın salındığı medyanın hangisi olduğu ve baskın medyadaki yarılanma ömrünün değerinin her türlü kalıcılık üzerine (birincil, ikincil, bütüncül kalıcılık) etkilerinin yüksek olduğu gözlenmiştir.

Anahtar Kelimeler: Bilgisayarlı Metotlar, Bütüncül Akıbet Modellemesi, Fizikokimyasal Tahmin Aracı, Öncelikli Kirleticiler, Transformasyon Ürünleri

To my family

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ABBREVIATIONS

ACP: Arctic Contaminant Potential

AD: Applicability Domain

Alachlor ESA: Alachlor Ethane Sulfonic Acid

Alachlor OXA: Alachlor Oxanilic Acid

BDE: Brominated Diphenyl Ether

BP: Diphenylmethanone

4-CBP: 4-chlorophenyl phenyl methanone

CFVP: Chlorfenvinphos

CP: Chlorpyrifos

CPO: Chlorpyrifos Oxon

CTD: Characteristic Travel Distance

DBF: Bis (4-chlorophenyl)methanone

1,3-DCB: 1,3-dichlorobenzene

DCM: Dichloromethane

DEA: 6-amino-2-chloro-4-isopropylamino-s-triazine

DIA: 6-amino-2-chloro-4-ethylamino-s-triazine

EPA: Environmental Protection Agency

EPI: Estimation Programs Interface

EU: European Union

FAV(s): Final Adjusted Value(s)

GLTE: Great Lake Transfer Efficiency

HA: 4-ethylamino-6-isopropylamino-2-hydroxy-s-triazine

HCBD: Hexachlorobutadiene

JP: Joint Persistence

LDV(s): Literature Derived Value(s)

LFERs: Linear Free Energy Relationships

LRTP: Long Range Transport Potential

LRAT: Long-Range Atmospheric Transport

MEHP: Mono-ethylhexyl Phthalate

MM model: Multimedia model

NPnEOs: Nonylphenol Ethoxylates

PA: Phthalic Acid

PBDEs: Polybrominated Diphenyl Ethers

PBT: Persistent, Bioaccumulative, Toxic

PCBs: Polychlorinated Biphenyls

PCBD: Pentachlorobutadiene

PEC: Predicted Environmental Concentration

PeCB: Pentachlorobenzene

PNEC: Predicted No-Effect Concentration

POPs: Persistent Organic Pollutants

PP: Primary Persistence

pp-LFERs: Poly-parameter Linear Free Energy Relationships

QSAR: Quantitative Structure-Activity Relationship

QSPR: Quantitative Structure-Property Relationship

SMILES: Simplified Molecular Input Line Entry System

SP: Secondary Persistence

sp-LFERs: Single parameter Linear Free Energy Relationships

SRC: Syracuse Research Corporation

TCM: Trichloromethane

TE: Transfer Efficiency

The EQC model: The Equilibrium Criterion model

TPs: Transformation Products

TP1Acl: 3-chloro-N1-hydroxy-4-phenoxybenzene-1,2-diamine

1, 3, 5-TCB: 1, 3, 5-trichlorobenzene

1, 2, 4-TCB: 1,2,4- trichlorobenzene

1, 2, 3, 5-TeCB: 1, 2, 3, 5-tetrachlorobenzene

1, 2, 4, 5-TeCB: 1, 2, 4, 5- tetrachlorobenzene

1, 2, 3, 4-TeCBD: 1, 2, 3, 4-Tetrachlorobutadiene

VP: Vapor Pressure

WFD: Water Frame Directive

WWTPs: Wastewater Treatment Plants

CHAPTER 1

INTRODUCTION

The number of chemicals used in commerce is exponentially increasing. Identifying the fate of these chemicals and their impact on the environment becomes a difficult task. MM models can integrate a variety of factors to investigate chemical concentrations and kinetics of transformation and transfer mechanisms in nature. Degradation rate constants, physicochemical properties of chemicals as well as information on emission are essential inputs for MM models (MacLeod et al., 2010). Indicators such as long-range transport potential (LRTP), characteristic travel distance (CTD), transfer efficiency (TE), and/or overall persistence (P_{ov}) of tested chemicals are typical outputs of MM models (Puzyn, 2011).

To conduct an alternative chemical assessment, the main challenge is to supply input parameters such as physicochemical property information. Traditional chemical testing necessitates a lot of time and money. A variety of models are present under computational methods for the estimation of physicochemical properties. Quantitative Structure-Activity Relationship/ Quantitative Structure-Property Relationship (QSAR/ QSPR) models estimate a chemical property as a function of molecular structure. High predictability using these models depends on the high quality of experimental data, and suitable molecular descriptors (Jagiello et al., 2015). QSAR models were suggested by Regulation for Registration, Evaluation, Authorisation, and Restriction of Chemicals to eliminate difficulties in traditional testing (Benfenati et al., 2011). In the last decades, poly-parameter linear free energy relationships (pp-LFERs) are also gaining favor (Goss & Schwarzenbach, 2001).

The integration of QSAR/QSPR or LFERs and MM models is becoming a new approach to evaluate the fate of an ever-increasing number of synthetic organic chemicals. Property estimation models can be applied in MM models, where physicochemical property information is unavailable, especially for the case of uncommon for transformation products (TPs).

While many studies emphasize the fate of parent compounds, studies generally ignore the effects of potential TPs on the overall fate of a compound. Indeed, TP formation causes higher spatial and temporal extents of chemical exposure. For instance, TPs can be detected more frequently than the main chemical (Kolpin et al., 2001). Additionally, TPs could be more toxic (Tixier et al., 2001) or persistent (Escher & Fenner, 2011) as compared to their parent compounds. If TPs are considered in persistence metric, it was stated that TPs could substantially increase the persistence (Fenner et al., 2003; Schenker et al., 2007).

In the EU Water Framework Directive (WFD) (2000), priority pollutants are identified as compounds that present considerable risk to the aquatic environment or via the aquatic ecosystem (Commission, 2000). Under this description, 45 priority substances are identified in Directive 2013/39/EU (Şıltu et al., 2017). To be a candidate for EU membership, Turkey adapted these priority pollutants into the national legislation by announcing Appendix 5 of Surface Water Quality Management Regulation in 2016.

Therefore, progress was made concerning national water quality management. However, only persistency determination for priority pollutants is not sufficient to protect public and environmental health. Simultaneously, the effects of TPs on the overall environmental fate of priority pollutants also need to be evaluated from a comprehensive water quality management perspective.

In the literature, possible treatment strategies have been investigated for priority pollutants that were stated in WFD (Belgiorno et al., 2007; Eriksson et al., 2007; Ribeiro et al., 2015). However, studying persistence assessment of priority pollutants via integrating their TPs has not been attempted before, to the best of the author's knowledge.

In this study, total of 14 organic chemicals within the priority pollutant list was selected. During selection, chemicals that are present in ionizable form under environmental pH values i.e. between 6 and 8 were removed, also metals were excluded. After these steps, the availability of scientific articles that include kinetic data and degradation pathway information, as well as those depicting clear molecular structure for parent compounds and their TPs were taken into consideration.

The overall aim of this study is to investigate the fate of selected priority chemicals and their TPs via the use of an evaluative MM model, namely the Equilibrium Criterion (EQC) model under steady-state and non-equilibrium conditions which is denoted as Level III. Specifically, this study aims to:

1. Compare the primary persistence of selected priority pollutants, secondary persistence for each transformation product, and joint persistence for the substance families.
2. Determine the relative environmental distribution of parent compounds and their TPs in air, water, soil, and sediment in a selected evaluative environment, as well as the impact of mode-of-entry, i.e. the input of chemical into each media, on this distribution.
3. Characterize prominent intermedia transport processes affecting the environmental distribution of substance families.
4. Identify input parameters (i.e. physicochemical property or degradation half-life) that have the greatest impact on primary and secondary persistence.

CHAPTER 2

LITERATURE REVIEW

As long as chemical diversity and amount increase with the predicted rate (UNEP, 2019), chemical pollution will challenge ecosystem services and human health (Diamond et al., 2015). Limited assimilative capacity of the Earth is the key issue in anthropogenic chemical based pollution. The challenge of chemical pollution management is regarding enormous numbers of chemicals, emitted from various sources, with highly fluctuating amounts in different parts of the world (Diamond et al., 2015). Figure 2.1 shows accelerating global chemical production compared to the global population.

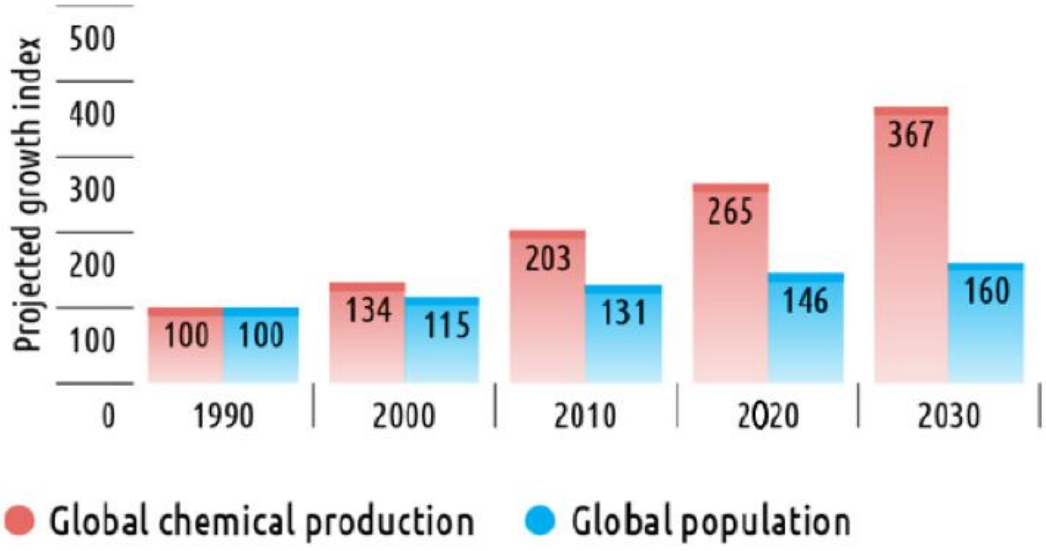


Figure 2.1. Growth of basic chemical production capacity versus population growth (UNEP, 2019).

Considering only one chemical is not sufficient to evaluate its fate due to possibility of other forms of other chemicals via degradation. Even though chemicals do not have toxic characteristics individually, their mixture could have significant toxic effects. According to the World Health Organization (2018), synthetic organic chemicals pose some risk to health regardless of their classification. Figure 2.2 indicates the possible effects of synthetic organic chemicals on health.

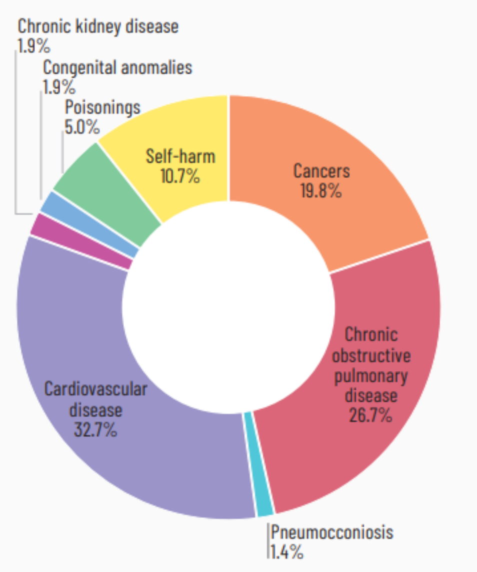


Figure 2.2. Percentage of chemical pollution based health problems (WHO, 2018).

Today, many categorizations exist for synthetic organic chemicals. Westerman (2007) summarized the various chemical classes and this summary is presented in Table 2.1. These types of classifications can ease chemical-based pollution management more effectively. Various chemicals are classified by considering a criterion such as toxicological mode of action, environmental properties, and so on. The second column of the summary table indicates a specific criterion for each of the chemical groups. Persistent Organic Pollutants (POPs), emerging contaminants, and priority pollutants will be explained in the following parts.

POPs are carbon-based chemical substances that are resistant to chemical, biological, or photolytic processes. In addition, they are capable of being transported a long distance, bioaccumulating in tissue, and biomagnifying in food chains. POPs may cause diabetes, obesity, cardiovascular problems, and hormone disruption (Alharbi et al., 2018). Also, certain cancers, birth defects, problems in immune and reproductive systems could occur in the case of POPs exposure (UNEP, 2017).

Table 2.1. Various Classification of Chemicals that was mainly retrieved from Westerman (2007).

Grouping	**Grouped According to**
EDC (Endocrine Disrupting Chemical) CMR (Carcinogenic, Mutagenic, Toxic to Reproduction)	Toxicological mode of action or endpoint
PBT (Persistent, Bioaccumulative, Toxic) vPvB (very Persistent, very Bioaccumulative) POP (Persistent Organic Pollutant)	Environmental Properties (e.g. ease of degradation or fat solubility)
PPCPs (Pharmaceuticals and Personal Care Products)	Type of intended usage
Priority Pollutants	Legislative enactment
Emerging Contaminants	Novelty, timeliness, or a new concern
HPV (High Production Volume Chemicals)	Manufactured or imported quantity
SVHC (Substance of Very High Concern)	Legislative enactment

In addition to POPs, emerging chemicals is another group that can be evaluated under micropollutants. An exact definition for emerging chemicals is challenging due to the relativity of “emerging”. However, they can be defined as a novel or traditional chemicals whose environmental effects have appeared or understood recently because of changing concerns. These materials could be persistent, toxic, bioaccumulative, endocrine disruptors, and have long-range atmospheric transport (LRAT) ability (Sauve & Desrosiers, 2014).

2.1 Priority Pollutants

Priority pollutant list can be considered to be a subgroup of micropollutants. The EU highlights the priority pollutants in Directive 2008/105/EC to come up with a solution for chemical pollution in the river basin (Pistocchi et al., 2019). The current list of all priority pollutants and selected ones that have (*) for this study are represented in Table 2.2. In this table, the members of HBCDD, PBDE, and dioxin groups are demonstrated clearly.

Table 2.2. Complete list of priority pollutants regulated under EU WFD.

Chemical Name	CAS Number	Chemical Name	CAS Number
Alachlor*	15972-60-8	Benzo(b)fluoranthene	205-99-2
Anthracene	120-12-7	Benzo(g,h,i)perylene	191-24-2
Atrazine*	1912-24-9	Benzo(k)fluoranthene	207-08-9
Benzene	71-43-2	Indeno(1,2,3-cd)pyrene	193-39-5
BDE 28	41318-75-6	Simazine	122-34-9
BDE 47	5436-43-1	Tributyltin compounds (Tributyltin-cation)	36643-28-4
BDE 99	60348-60-9	Trichlorobenzenes	12002-48-1
BDE 100	189084-64-8	Trichloromethane (chloroform)*	67-66-3
BDE 153*	68631-49-2	Trifluralin*	1582-09-8
BDE 164	207122-15-4	Dicofol*	115-32-2
Chloroalkanes, C10-13 iv	85535-84-8	PFOS	1763-23-1
Chlorfenvinphos*	470-90-6	Quinoxyfen	124495-18-7
Chlorpyrifos*	2921-88-2	2,3,7,8-T4CDD	1746-01-6
1,2-Dichloroethane	107-06-2	1,2,3,7,8-P5CDD	40321-76-4
Dichloromethane	75-09-2	1,2,3,4,7,8-H6CDD	39227-28-6
DEHP*	117-81-7	1,2,3,6,7,8-H6CDD	57653-85-7
Diuron*	330-54-1	1,2,3,7,8,9-H6CDD	19408-74-3
Endosulfan	115-29-7	1,2,3,4,6,7,8-H7CDD	35822-46-9
Fluoranthene	206-44-0	1,2,3,4,6,7,8,9-08CDD	3268-87-9
Hexachlorobenzene	118-74-1	Aclonifen*	74070-46-5
Hexachlorobutadiene*	87-68-3	Bifenox*	42576-02-3
Hexachlorocyclohexane	608-73-1	Cybutryne	28159-98-0
Isoproturon	34123-59-6	Cypermethrin	52315-07-8
Naphthalene	91-20-3	Dichlorvos	62-73-7
Nonylphenols	84852-15-3	1,2,5,6,9,10-hexabromocyclododecane	3194-55-6
Octylphenols	140-66-9	Alpha-hexabromocyclododecane	134237-50-6
Pentachlorobenzene*	608-93-5	Beta-hexabromocyclododecane	134237-51-7
Pentachlorophenol	87-86-5	Gama-hexabromocyclododecane	134237-52-8
Benzo(a)pyrene	50-32-8	1,3,5,7,9,11-hexabromocyclododecane	25637-99-4
Terbutryn	886-50-0	Heptochlor epoxide	76-448/1024-57-3

Directive 2008/105/EC and Directive 2013/39/EU are the EU legislations that are linked to the EU WFD. They cover priority chemical administration in surface waters regarding coastal, inland, and transitional waters.

In the EU WFD (2000), priority pollutants were determined compounds that present considerable risk to the aquatic environment or via the aquatic ecosystem. A total of 45 priority substances were announced in Directive 2013/39/EU (Şıltu et al., 2017).

These pollutants have to be monitored and identification of water bodies must be done regarding environmental quality standards (Pistocchi et al., 2019).

As a candidate for EU membership, integrated studies are being conducted for watershed specific pollutants and environmental quality standards (Şıltu et al., 2017). Furthermore, a total of 45 priority substances were integrated into the Surface Water Quality Management Regulation in Turkey. Apart from the priority compounds indicated in the previous table with an asterisk, p,p'-DDT was also studied because of p,p'-DDT level in dicofol as an impurity.

2.2 Concerns About Priority Pollutants and Their Transformation Products

Persistence is the residence time in a multimedia environment under steady-state conditions. Even though different nations set various criteria about chemical prioritization, a medium-specific half-life approach for persistence was suggested by Canada. This approach could be considered internationally acceptable (Webster et al., 1998). According to this approach, the persistence of the chemical is determined regarding merely half-life in an environmental compartment.

According to the definition by the Stockholm Convention on Persistent Organic Pollutants, a chemical is labeled as persistent if its half-life in water exceeds two months, or its half-life in soil is greater than six months, or its half-live in sediments is greater than six months (Stockholm Convention, 2009). This type of chemical assessment does have its drawbacks, as argued by Webster et al (1998). The first drawback is that half-life measurement could change according to conditions where half-life is measured. The second drawback is that the partitioning effect and mode-of-entry are ignored in medium based half-live determination (Webster et al., 1998). Hence, usage of Level III- type mass balance multimedia model was suggested to regard partitioning and transport mechanisms (Webster et al., 1998).

Due to resistance to transformation, some chemicals might stay in the environment for many years. Therefore, they could migrate extensively in the environment and reach susceptible receptors. Also, persistence could result in the accumulation of a chemical in high amounts in the environment. Because chemical mass in the environment is calculated via multiplying the emission rate by residence time.

Even if the emission of a persistent chemical is stopped, the removal of this chemical from the environment could be retarded because of its persistent nature (Mackay, 2001). Additionally, the chemical amounts could affect the well-being of the public and ecosystems. It is not possible to directly measure the persistence of chemicals by any type of monitoring effort (Fenner et al., 2005), because chemical degradation can be affected by several factors. The environmental degradation rate depends on many criteria such as environmental medium, temperature, presence of sunlight, nature, and number of degrading organisms, acidity, availability of reactants, and catalysts availability. That’s why environmental persistence cannot be understood regarding radioisotopes that have fixed and media-independent half-lives. A chemical compound has a spatially varying distribution of half-lives rather than having one value in the environment (Mackay, 2001).

In spite of challenging determination of persistence, it is one of the factors that is employed for priority setting in chemical assessment (Mackay, 2001). Therefore, multimedia fate models are a tool to determine chemical persistence in the environment (Fenner et al., 2005).

Persistence, namely a hazard metric causes difficulty in the assessment. Because half-lives and degradation pathways of chemicals are highly variable. They might not be properly characterized (Ng et al., 2011). Evaluation of TPs could not be feasible providing that the high cost of only parent compound screening (Ng et al., 2011).

TPs could influence chemical pollution. Monitoring studies on TPs are rare and they mainly focus on well-known TPs of pesticides (Fenner et al., 2009). Because of restricted time and sources, high-quality data on substance properties and comprehensive risk assessment are not available for TPs. Therefore, screening approaches propose prioritizing TPs before further assessment.

Environmental fate modeling of TPs allows determining the likelihood of TPs in environmental media. According to Fenner and colleagues (2009), TPs fate models could be categorized into three classes. The first class is models that rank a large group of TPs regarding risk. The second class is multispecies multimedia models. The last one is simulative models that estimate real environmental concentration by mimicking site-specific conditions.

Although some TPs might be more common than the parent compound, TPs are typically not measured in the environment. Therefore, humans might be exposed to a variable and unknown chemical cocktail. Synergistic effects (i.e. presence of parent compound with its TPs simultaneously) could complicate chemical risk assessment (Escher & Fenner, 2011).

Persistence, mobility, toxicity, and high generation yield of TPs can increase risks of the parent compound significantly. Providing insufficient data, assessment of parent compound relative to its TPs can be done by using generic models (Escher & Fenner, 2011).

Priority pollutant list includes various types of pesticides, solvents, and industrial chemicals. To degrade recalcitrant pesticides, advanced oxidation processes (AOPs) such as photocatalytic ozonation is applied (Farré et al., 2005). In addition to pesticide degradation, the TiO_2-mediated photocatalytic mechanism is the best way for polybrominated diphenyl ethers (PBDEs). Hence, the formation of congeners with fewer bromine atoms and mineralization is possible (Pan et al., 2016). In the case of priority pollutant degradation, the dominant mechanism might change depending on environmental media. For example, photodegradation is the prominent mechanism for DEHP in the atmosphere, but biodegradation could become a dominant mechanism in soil, surface water, and sediment (Staples et al., 1997).

The chemistry of the query compound in the priority pollutant list and the chemistry of the receiving environment affect the fate of the investigated substance family (Graham et al., 1999). Biological transformation of pesticides to one or multiple TPs usually generates undiscovered effects (Novak et al., 1997). Moreover, pesticide transformation in aquatic ecosystems leads to form TPs that have a similar or higher risk compared to parent pesticide (Belfroid et al., 1998). Pesticides are a major contributor to priority pollutants, so it can be said that the transformation of priority pollutants may generate more adverse undetermined effects on the environment compared to their parent compound.

2.3 Multimedia Fate Modeling

MM models are based on the mass balance principle. Transport and transformation mechanisms in several compartments are mimicked by the multimedia approach. Risk assessment, management, optimization of testing and monitoring methods, and chemical ranking studies could employ MM models. Emission rates and relative environmental concentration in various media could be obtained from these models (Valsaraj, 2009). Also, other outputs such as P_{ov} and LRTP can be acquired from MM models.

MM models have been categorized regarding their LRTP metric as either transport-oriented or target-oriented ones. Transport oriented ones describe probable transportation in mobile phases (i.e. air or water) with a concurrent exchange with surface media. On the other hand, target-oriented multimedia models describe a percentage of emitted chemicals that transport to a specific region as a result of transport in mobile phases and following depositions into other media (Fenner et al., 2005). Examples for transport based metrics are spatial range and CTD. The spatial range indicates the distance that includes 95% of the area under plotting concentration versus distance curve (Scheringer, 1996). CTD defines the point in the space where the concentration decreases the approximately %37 of the initial value (Bennett et al., 1998). Arctic Contaminant Potential (ACP) and Great Lake Transfer

Efficiency (GLTE) are examples of target-oriented LRTP metrics. ACP defines the ratio between the present amount of chemical in the Arctic surface after 10 years and the emission amount during these 10 years (Wania, 2003). GLTE demonstrates the ratio of the deposition mass flux from air to water in the Great Lakes Basin and emission flux (MacLeod & MacKay, 2004).

Several multimedia models satisfy diverse research questions and determine the fate of many query compounds. Assumptions, geometry, model structures, a metric definition for LRTP can vary between the models. For example, the number of environmental phases, regional characteristics, and spatial scales are model-specific factors (Fenner et al., 2005).

The key point is to consider the physicochemical properties of a query compound when selecting the best multimedia model for fate assessment of this query compound. Model properties and parametrization could be significant phenomena for fate determination under four categorizations of chemicals. For chemicals with low volatility, high solubility and high half-life in water, they are significantly affected by the existence of transportation and mechanism types in the water. For chemicals that tend to stick on aerosols, an assumption about the degradability of aerosol-bound fraction is important. Particle settling to the deep sea might reduce LRTP of a chemical if chemical high octanol-water partition coefficient with low air-water partition coefficient. Lastly, the type of LRTP metric (i.e. transport-oriented or target-oriented one) could be critical for very volatile chemicals (Fenner et al., 2005).

Environmental fate models are run to integrate degradation and partitioning of a chemical, emission scenarios to determine chemical distribution and fluxes in the multimedia environment. Model developments in different temporal and spatial scales, improvement in chemical property estimation, determination of emission data, the addition of environmental media, and processes were some changes within the past 25 years. Despite these improvements, the prediction of the partitioning coefficient for polar & ionizable chemicals, realism about the ecosystem, and definition of the bioavailability term stay as challenges (Di Guardo et al., 2018).

2.4 Properties and History of the EQC Model

The EQC model is an evaluative fugacity based multimedia model. The fugacity concept in environmental systems was introduced in 1979 by Donald Mackay as an indicator of the likely behavior of a toxic compound (Mackay, 1979). This type of chemical modeling aims to establish general characteristics of chemical behavior such as where a chemical is likely to partition, what is the primary loss mechanism, and persistence. Hence, this type of evaluation could be enough to decide whether authorities should be further concerned with this compound or not. Nonetheless, the model does not aim to simulate the fate and transport of chemicals in a real environment. It is an evaluative model. Furthermore, how much time should pass to reach a predetermined concentration cannot be understood from the EQC model (Mackay et al., 1996a).

The EQC model has been used for several purposes. Palm et al. (2002) utilized a six-stage methodology to investigate the possible fate and research needs for PBDEs (Palm et al., 2002). The EQC model with experimental, calculated inputs and EPI Suite predicted ones were utilized to evaluate their fate. In another study that was conducted by Achten et al. (2002), the fate of methyl tert-butyl ether in selected environmental compartments (air and water) were evaluated considering generic conditions and user-defined environmental inputs. The mass distribution between air and water phase was interpreted regarding the main transport mechanism and mode-of-entry effect (Achten et al., 2002). The EQC model can also be used as an assessment, prediction, and review tool for physicochemical properties, emission rates, and monitoring studies, respectively (Cousins et al., 2002). For example, to indicate the effects of various organic carbon water partitioning coefficients (K_{oc}) for volatile methyl siloxanes on their persistence, a region-specific model, and EQC model were run (Panagopoulos & MacLeod, 2018).

To determine the fate of nonvolatile chemicals, vegetation compartment was added to four environmental compartments namely air, water, soil, and sediment. Therefore, the fate of three pesticides was compared by using modified EQC (i.e. including vegetation compartment) and the EQC model (Batiha et al., 2009).

In addition to fate modeling, the effects of chemical exposure can be analyzed by determining the environmental concentration of a chemical. For instance, screening level based risk evaluation was conducted by integrating the EQC and a straightforward biouptake model. Hence, chemical transport from emission to a receiver and internal body concentrations were predicted by the EQC and biouptake model, respectively (Macleod et al., 2004).

The first version of the EQC model that was generated in 1996 categorized chemicals such as multimedia substances, nonvolatile chemicals, and insoluble ones concerning their physicochemical properties (Mackay et al., 1996a). This chemical classification was removed in the updated EQC model that was introduced in 2012 (Hughes et al., 2012). The most recent version of the model is converted into an MS Excel spreadsheet format. Mandatory theoretical and empirical equation based partitioning coefficients were eliminated, so users can put their own partition coefficients. However, some partition coefficient can be kept in case of user preference. Easiness in sensitivity, uncertainty analysis, and flexibility in input adjustment, such as including temperature effect was enabled (Hughes et al., 2012).

The EQC model contains Level I, Level II, and Level III type of multimedia fate evaluations. It has completely mixed four main environmental compartments namely, air, water, soil, and sediment with predetermined dimensions. While Level I symbolizes an evaluative environment as steady-state, and equilibrium without degradation, Level II type includes degradation and advection. In addition to degradation and advection, intermedia transfer was considered in Level III under non-equilibrium and steady-state conditions. Figure 2.3 represents the EQC model in a diagram format.

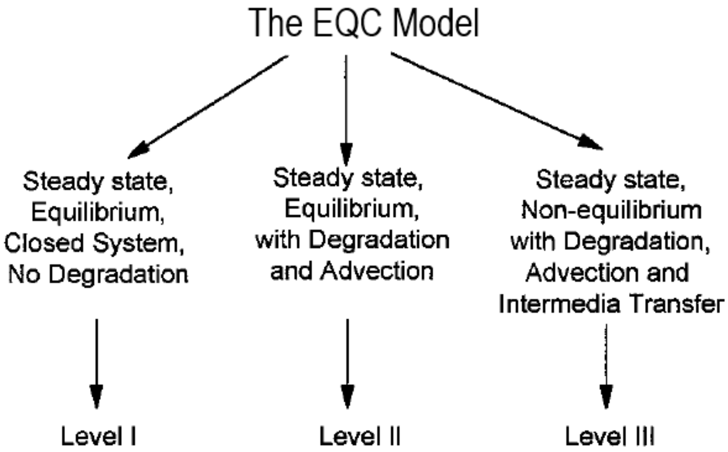


Figure 2.3. The EQC Model with Level I, Level II, Level III. This figure was mainly adapted/ retrieved from Mackay et al. (1996a).

2.5 Physicochemical Estimation Methods such as QSARs and LFERs

There are two methodologies embodied in physicochemical estimation tools. The first one is that molecular descriptors can be formed by structure-based computational tools. Then, the number of descriptors could be reduced by statistical tools. Later, linear regression or non-linear equation-based models use the descriptors to estimate physicochemical properties. The second one is that less flexible models calculate a small number of descriptors and then use these descriptors for physicochemical estimation (Poole et al., 2013). QSPR/QSAR and LFERs are the main physicochemical property estimation tools.

QSPR/QSAR is a quantitative relationship between a physicochemical property/ biological activity and the molecular structure of a chemical (OECD, 2007). QSAR models have been improved from simple regression on small descriptors to several statistical and machine learning methods on diverse chemicals (Cherkasov et al., 2014).

LFER is a linear relationship that predicts phase partition constants regarding interactions between the chemical and organic phases (Nguyen et al., 2005). Single parameter LFERs were criticized that only a single parameter cannot provide accurate identification of molecular interactions (Goss & Schwarzenbach, 2001). The most significant solute-phase intermolecular interactions for energy contributions are considered to predict partitioning coefficients in poly-parameter LFERs (Tülp et al., 2008).

EPI Suite

The minimum information required of a chemical for pre-manufacture notice is not sufficient to allow the manufacturer to produce this chemical. In such a case, U.S. Environmental Protection Agency (EPA) developed chemical property estimation tools such as QSARs to fill data gaps in physicochemical properties, fate, and toxicity of chemicals. In addition to the benefit of QSARs for decision-makers, these tools are being implemented in case of new chemical development, design of industrial processes, monitoring studies, and improving laboratory analysis. U.S. EPA contracted Syracuse Research Corporation (SRC) to improve chemical data compilation and analysis. After many inputs had been estimated by individual programs, they were integrated under the name of Estimation Programs Interface (EPI). SRC converted EPI to a format that was suitable for Microsoft Windows operating system. Then, U.S. EPA bought EPI’s copyright from SRC and changed the name of the program as EPI Suite. EPI Suite could be freely downloaded from the website of the U.S. EPA. It could supply input data for several models such as other U.S. EPA models as well as multimedia models to assess chemicals. EPI Suite is an integrated QSAR that includes many sub-estimation programs (Card et al., 2017).

EPI Suite utilizes a fragmentation method. In this methodology, the molecular structure is broken into fragment series and each fragment is multiplied with relevant assigned descriptor value. Then, fragmented values are integrated into each other to obtain chemical-specific property (Poole et al., 2013). Melting point, boiling point, vapor pressure, partitioning coefficients, atmospheric oxidation rate, hydrolysis rate, aerobic/anaerobic degradability, bioconcentration/bioaccumulation factors, and removal of chemical in the wastewater treatment plant and partitioning in various environmental compartments could be the output of EPI Suite just utilizing the chemical name, CAS number or Simplified Molecular Input Line Entry System (SMILES) notation of a chemical. Despite various property estimation, it could not work very well for inorganic, organometallic, very large molecules, and some ionizable organic compounds. Like other property estimation models, the ultimate aim of EPI Suite is to screen a large number of chemicals that have various structures and properties (Card et al., 2017).

2.6 Fate Determination by Combining Physicochemical Estimation Tools (QSAR Models) and Multimedia Models

Jagiello and coworkers (2015) underlined that combination QSAR/QSPR models or pp-LFERs and MM models show promise with respect to risk management concerning chemicals. To test the effect of predicted inputs, Puzyn (2011) examined P_{ov} and LRTP estimation of an MM model that uses experimental and predicted property information. The chief result of this study was that there was no statistical difference between the two (Puzyn, 2011). Apart from the integration of QSPR with MM models, a combination of pp-LFER with MM was suggested in place of single parameter-LFERs (sp-LFERs). Authors underlined the limitations of model parametrization as well as the impact of the use of sp-LFER or pp-LFERs (Breivik & Wania, 2003).

Applicability Domain (AD) is a hypothetical space that is bordered by structural similarity and range of endpoints. Predictions are credible only if chemicals are located in the applicability domain (Gramatica, 2007). Furthermore, many chemicals have complicated partitioning tendencies. Extending AD could be achieved by adding experimental partitioning coefficients, multiple sp-LFER equations, or pp-LFERs integration to multimedia models. The last option can allow for assessing several types of chemicals with polar functional groups (Breivik & Wania, 2003). For example, Zukowska and colleagues (2006) investigated three pharmaceuticals by implementing a pp-LFER based MM model. After the model was parameterized with respect to a real drainage basin, the chemical-based input requirement was satisfied by the EPI Suite and the literature (Zukowska et al., 2006). In addition to being able to model relatively polar chemicals, additional phases could also be considered without additional input requirements (Breivik & Wania, 2003) by coupling MM models with property estimation tools. Also, pp-LFER based models can supply mechanistic perspectives in several interactions (Zukowska et al., 2006). The results of pp-LFER based and sp-LFER based MM models are not significantly different as compared to model parametrization. Therefore, Brown et al. (2009) recommended that the selection of sp-LFER or pp-LFER depended on the availability of input parameters. They evaluated that this was increasingly becoming possible owing to increasing available data (Brown & Wania, 2009). QSPR-MM modeling is evaluated as reasonable as long as a stronger association between modelers and experimentalists can be maintained (Jagiello et al., 2015).

Integrated modeling studies that investigate the fate of chemicals with their TPs were searched in the literature excluding toxicity studies. These studies are presented in chronological order in the next table.

Table 2.3. Integrated fate modeling studies on chemicals with their TPs.

The name of the study	**Study Aim**	**Methodology**	**Chemicals**	**Overall Remarks**	**Reference**
Persistence of Parent Compounds and Transformation Products in a Level IV Multimedia Model	To show residence time in steady-state condition and residence time in a pulse emission by introducing joint persistence and secondary persistence concept	The generic three-box model with experimental property values	Atrazine with deisopropyl atrazine and methyl tert-butyl ether with tert-butyl alcohol	Secondary persistence can be used in exposure-based ranking between TPs that are from the same parent compound.	(Fenner et al., 2000)
Including Transformation Products into the Risk Assessment for Chemicals: The Case of Nonylphenol Ethoxylate Usage in Switzerland	To conduct a risk assessment using the ratio between predicted environmental concentration (PEC) and predicted no-effect concentrations (PNEC)	For PECs, the regional Level III model was adjusted to represent Switzerland. For PNEC, acute toxicity data sets on nonylphenol ethoxylates (NPnEOs) and its TPs were assessed.	NPnEOs and their TPs	In risk assessment of a specific chemical, the number of TPs that are included in the assessment is important.	(Fenner et al., 2002)

Table 2.3. (Cont‘d).

The name of the study	**Study Aim**	**Methodology**	**Chemicals**	**Overall Remarks**	**Reference**
Joint Persistence of Transformation Products in Chemicals Assessment: Case Studies and Uncertainty Analysis	To indicate the effects of TPs on persistency To compare JP and PP of the parent compound	The generic three-box multimedia model with literature derived properties	NPnEOs, perchloroethylene, and atrazine with their TPs	TPs could substantially increase persistence.	(Fenner et al., 2003)
Including Degradation Products of Persistent Organic Pollutants in a Global Multi-Media Box Model	To analyze the significance of TPs in fate models To include TPs into current exposure-based hazard indicators	Modified CliMoChem with literature derived degradation pathways and chemical properties with some predicted degradation scheme and chemical properties	Five pesticides	JP, spatial range, and ACP increase significantly if TPs are included. However, an increase in persistence could not cause a corresponding increase in spatial range.	(Schenker et al., 2007)
Indicators for the Exposure Assessment of Transformation Products of Organic Micropollutants	To improve the process-based model with indicators that demonstrate the fate of parent compounds and their TPs quantitatively	A generic three-box global MM model was used. Transformation schemes, some chemical properties, ff^{xy} formation were compiled from the literature. Remaining inputs from EPI Suite	16 pesticides and relevant TPs	JP indicator and relative aquatic concentration prove the significance of TPs in PBT assessment and future water monitoring programs, respectively.	(Gasser et al., 2007)

CHAPTER 3

MATERIALS AND METHODS

The applied methodology aims for a comprehensive persistence evaluation of the selected chemicals. To do this, their TPs are included using a joint persistence concept, as introduced by Fenner et al. (2003). Advection eliminated Level III module of the EQC model was run for all compounds. Input requirements of the EQC model were provided via literature review, and EPI Suite^{TM} v4.11, June 2017. After physicochemical property and degradation half-life information was compiled, a thermodynamic consistency check of physicochemical properties was conducted, followed by adjustment for predicted literature derived values (LDVs), experimental LDVs, and EPI Suite predicted ones.

3.1 Selected Chemicals and Their Transformation Products

In this study, a total of 14 organic chemicals from the EU WFD priority pollutant list was selected. The selection was done within priority pollutants by considering data availability. Additionally, p,p'-DDT was added to this chemical list because of the p,p'-DDT level in dicofol as an impurity.

During selection, chemicals that are present in an ionizable form in environmental pH values i.e. between 6 and 8, as well as metals were excluded. After these steps, for the rest of the compounds in the priority pollutant list, a thorough literature search was performed. The availability of scientific articles that include kinetic data and degradation pathways, together with a clear molecular structure for parents and compounds that are produced as a result of degradation studies was considered. During the selection of TPs, predictive softwares were excluded on purpose. That is, only TPs that were experimentally shown to be formed from the parent compounds are considered in this study. Furthermore, as much as possible, at least two scientific articles were sought for, in order to identify a TP. For some chemical families, only one article was used due to limited scientific literature on the topic. Articles that contain the molecular structure of all TPs were used to obtain SMILES notation for EPI Suite. Furthermore, a specific degradation pathway such as only photolysis, or biological degradation was not selected. The sole criterion was for the degradation scheme to be shown to occur under laboratory or field conditions. Lastly, the number of sequences of TPs, in other words, the generation of products was another issue of concern. Typically two generations of TPs were tried to be considered, however for the case of PBDEs, more were included because of availability and clear depiction of degradation schemes. On the other hand, only one generation of TPs could be identified for some compounds. The list of parent compounds with their CAS numbers is represented in Table 3.1. Selected TPs with their parent compounds are indicated in Table 3.2.

.Table 3.1. Evaluated compounds in this study with their CAS number & usage area

Substance	CAS Number	Type	Substance	CAS Number	Type
Atrazine	1912-24-9	P	Bifenox	42576-02-3	P
DEHP	117-81-7	I	Pentachlorobenzene (PeCB)	608-93-5	S
Dicofol	115-32-2	P	Trichloromethane	67-66-3	S
p,p'-DDT	50-29-3	P	Aclonifen	74070-46-5	P
Chlorpyrifos	2921-88-2	P	BDE-153	68631-49-2	I
Trifluralin	1582-09-8	P	Diuron	330-54-1	P
Alachlor	15972-60-8	P	Hexachlorobutadiene (HCBD)	87-68-3	S
Chlorfenvinphos (CFVP)	470-90-6	P			

P: Pesticide, I: Industrial Chemical, S: Solvent

Table 3.2. Selected TPs with their parent compounds that are bold.

Atrazine	**Trifluralin**
DEA	TR-7
DIA	TR-9
HA	TR-4
Diuron	**Chlorpyrifos (CP)**
DCPMU	Chlorpyrifos oxon (CPO)
MCPDMU	TCP
DCPU	**BDE-153**
DCA	BDE-101
Alachlor	BDE-99
Lactam	BDE-118
Alachlor ESA	BDE-52
Alachlor OXA	BDE-49
DEHP	BDE-47
MEHP	BDE-66
PA	BDE-77
Dicofol	**Pentachlorobenzene (PeCB)**
bis(4-chlorophenyl)methanone (DBF)	1,2,3,5-TeCB
4-chlorophenyl phenyl methanone (4-CBP)	1,2,4,5-TeCB
diphenylmethanone (BP)	1,3,5-TCB
p,p'-DDT	1,2,4-TCB
p,p'-DDE	1,3-DCB
p,p'-DDD	**Chlorfenvinphos (CFVP)**
p,p'-DDNU	Desethyl-chlorfenvinphos
	2,4-dichlorophenacyl chloride
	1-(2,4-dichlorophenyl) ethane-1,2-diol

3.2 The EQC Model

Unlike other multimedia fate models, the EQC model can assess the fate of several chemicals that have different partitioning tendencies (Mackay et al., 1996a). That's why the EQC model was selected for chemicals that are used for various purposes and are a member of different chemical groups. EQC Version 4.00 downloaded from Trent University Chemical Properties Research Group web page (https://tuspace.ca/~mparnis/Models.html) was used in this study.

Although the EQC model includes Level I, Level II, and Level III with increasing complexity, only Level III submodule was utilized in this study excluding 4.1.3 subsection. Level III regards steady-state and non-equilibrium conditions, including degradation, advection, and intermedia transfer mechanisms. The effects of advection processes were eliminated from the evaluative environment to consider a chemical loss because of only reactions. In case of advective losses, less residence time is observed and this causes a mistake in persistence. Advective losses change the location of chemicals, but they are still present in the global system (Webster et al., 1998).

Chemical Concentration Calculation

All stated equations in the section were retrieved from Mackay, 2001.

Concentration is the product of fugacity and proportionality constant, as indicated below.

$$\mathrm{C} = \mathrm{Z} \times \mathrm{f} \tag{3.1}$$

C: Concentration in the compartment (mol/m^3)

Z: Proportionality constant in the compartment (mol/m^3×Pa)

f: Fugacity (Pa)

In the first step, fugacity is determined by considering utilized environmental transport, transfer, and transformation mechanisms. In the case of advection, degradation, and intermedia transport processes, separate transport parameters (D) with a unit of mole/Pa×h are calculated.

For Advection:

$$\mathrm{D} = \mathrm{G} \times \mathrm{Z} \tag{3.2}$$

D: Transport parameter for advection (mole/Pa×h)

G: Flow rate (m^3/h)

$$\mathrm{I} = \mathrm{E} + \mathrm{G_A C_{BA}} + \mathrm{G_W C_{BW}} \tag{3.3}$$

$$\mathrm{f} = \frac{\mathrm{I}}{\sum \mathrm{G_i Z_i}} \tag{3.4}$$

I: Total influx (mole/h)

E: Emission rate (mole/h)

C_{BA}, C_{BW}: The concentration of B chemical in air and water compartment, respectively (mole/m^3)

i: environmental medium

For Degradation:

$$\Sigma D_R = \Sigma V_i Z_i k \tag{3.5}$$

D_R: Transport parameter for degradation (mole/Pa×h)

V_i: Volume of compartment i (m^3)

k: Degradation rate (1/h)

$$f = \frac{E}{\Sigma D_R} \tag{3.6}$$

For Intermedia Transport:

There are twenty-one different D values between air, water, soil, and sediment compartments to indicate diffusion, rain dissolution, wet deposition, dry deposition, surface runoff, sediment deposition, and resuspension. Their briefly compiled form is below.

Air (1)- Water (2)

$$D_{12} = D_v + D_{RW2} + D_{QD2} + D_{QW2} \tag{3.7}$$

$$D_{21} = D_V \tag{3.8}$$

Air (1)- Soil (3)

$$D_{13} = D_E + D_{RW3} + D_{QW3} + D_{QD3} \tag{3.9}$$

$$D_{31} = D_E \tag{3.10}$$

Soil (3)- Water (2)

$$D_{32} = D_{SW} + D_{WW} \tag{3.11}$$

Sediment (4)- Water (2)

$$D_{42} = D_Y + D_{RS} \tag{3.12}$$

$$D_{24} = D_Y + D_{DS} \tag{3.13}$$

D_V: Diffusive absorption between air and water (mole/Pa×h)

D_{RW2}: Rain wet dissolution to water (mole/Pa×h)

D_{QD2}: Aerosol dry deposition to water (mole/Pa×h)

D_{QW2}: Aerosol wet deposition to water (mole/Pa×h)

D_E: Diffusive absorption between air and soil (mole/Pa×h)

D_{RW3}: Rain wet dissolution to soil (mole/Pa×h)

D_{QD3}: Aerosol dry deposition to soil (mole/Pa×h)

D_{QW3}: Aerosol wet deposition to soil (mole/Pa×h)

D_{SW}: Soil runoff to water medium (mole/Pa×h)

D_{WW}: Water runoff to water medium (mole/Pa×h)

D_Y: Diffusion absorption between sediment and water (mole/Pa×h)

D_{DS}: Deposition of sediment (mole/Pa×h)

D_{RS}: Resuspension of sediment (mole/Pa×h)

Level III Equations

According to mass balance, entered mass to the environment must be equal to mass loss from the environment. Indices in 1, 2, 3, and 4 represent air, water, soil, and sediment, respectively.

Air

$$E_1 + G_{A1}C_{B1} + f_2D_{21} + f_3D_{31} = f_1(D_{12} + D_{13} + D_{R1} + D_{A1}) \\ = f_1D_{T1} \tag{3.14}$$

E_1: Emission rate into air (mole/h)

G_{A1}: Advective inflow rate to air (m^3/h)

C_{B1}: The concentration of chemical B in air (mole/m^3)

f_2: Fugacity in water (Pa)

D_{21}: Intermedia transport rate from water to air (mole/Pa×h)

f_3: Fugacity in soil (Pa)

D_{31}: Intermedia transport rate from soil to air (mole/Pa×h)

f_1: Fugacity in air (Pa)

D_{12}: Intermedia transport from air to water (mole/Pa×h)

D_{13}: Intermedia transport rate from air to soil (mole/Pa×h)

D_{R1}: The reaction rate in air (mole/Pa×h)

D_{A1}: Advection rate in air (mole/Pa×h)

D_{T1}: The sum of all loss D values from medium air (mole/Pa×h)

Water

$$E_2 + G_{A2}C_{B2} + f_1D_{12} + f_3D_{32} + f_4D_{42} \\ = f_2(D_{21} + D_{24} + D_{R2} + D_{A2}) = f_2D_{T2} \tag{3.15}$$

E_2: Emission rate into water (mole/h)

G_{A2}: Advective inflow rate to water (m^3/h)

C_{B2}: The concentration of chemical B in water (mole/m^3)

f_1: Fugacity in air (Pa)

D_{12}: Intermedia transport rate from air to water (mole/Pa×h)

f_3: Fugacity in soil (Pa)

D_{32}: Intermedia transport rate from soil to water (mole/Pa×h)

f_4: Fugacity in sediment (Pa)

D_{42}: Intermedia transport from sediment to water (mole/Pa×h)

f_2: Fugacity in water (Pa)

D_{21}: Intermedia transport from water to air (mole/Pa×h)

D_{24}: Intermedia transport from water to sediment (mole/Pa×h)

D_{R2}: The reaction rate in water (mole/Pa×h)

D_{A2}: Advection rate in water (mole/Pa×h)

D_{T2}: The sum of all loss D values from medium water (mole/Pa×h)

Soil

$$E_3 + f_1 D_{13} = f_3(D_{31} + D_{32} + D_{R3}) = f_3 D_{T3} \tag{3.16}$$

E_3: Emission rate into soil (mole/h)

f_1: Fugacity in air (Pa)

D_{13}: Intermedia transport rate from air to soil (mole/Pa×h)

f_3: Fugacity in soil (Pa)

D_{31}: Intermedia transport rate from soil to air (mole/Pa×h)

D_{32}: Intermedia transport rate from soil to water (mole/Pa×h)

D_{R3}: The reaction rate in soil (mole/Pa×h)

D_{T3}: Sum of all loss D values from medium soil (mole/Pa×h)

Sediment

$$E_4 + f_2 D_{24} = f_4(D_{42} + D_{R4} + D_{A4}) = f_4 D_{T4} \tag{3.17}$$

E_4: Emission rate into sediment (mole/h)

f_2: Fugacity in water (Pa)

D_{24}: Intermedia transport rate from water to sediment (mole/Pa×h)

f_4: Fugacity in sediment (Pa)

D_{42}: Intermedia transport rate from sediment to water (mole/Pa×h)

D_{R4}: The reaction rate in sediment (mole/Pa×h)

D_{A4}: Advection rate in sediment (mole/Pa×h)

D_{T4}: The sum of all loss D values from medium sediment (mole/Pa×h)

Four unknown fugacity values can be solved by four equations. Since the number of the equation are equal to the number of unknowns, a solution is possible.

$$f_2 = (I_2 + \frac{J_1 J_4}{J_3} + \frac{I_3 D_{32}}{D_{T3}} + \frac{I_4 D_{42}}{D_{T4}}) / (D_{T2} - \frac{J_2 J_4}{J_3} - \frac{D_{24} D_{42}}{D_{T4}}) \tag{3.18}$$

$$f_1 = \frac{(J_1 + f_2 J_2)}{J_3} \tag{3.19}$$

$$f_3 = \frac{(I_3 + f_1 D_{13})}{D_{T3}} \tag{3.20}$$

$$f_4 = \frac{(I_4 + f_2 D_{24})}{D_{T4}} \tag{3.21}$$

Where,

$$J_1 = \frac{I_1}{D_{T1}} + \frac{I_3 D_{31}}{(D_{T3} D_{T1})}$$

$$J_2 = \frac{D_{21}}{D_{T1}}$$

$$J_3 = 1 - \frac{D_{13} D_{31}}{(D_{T3} D_{T1})}$$

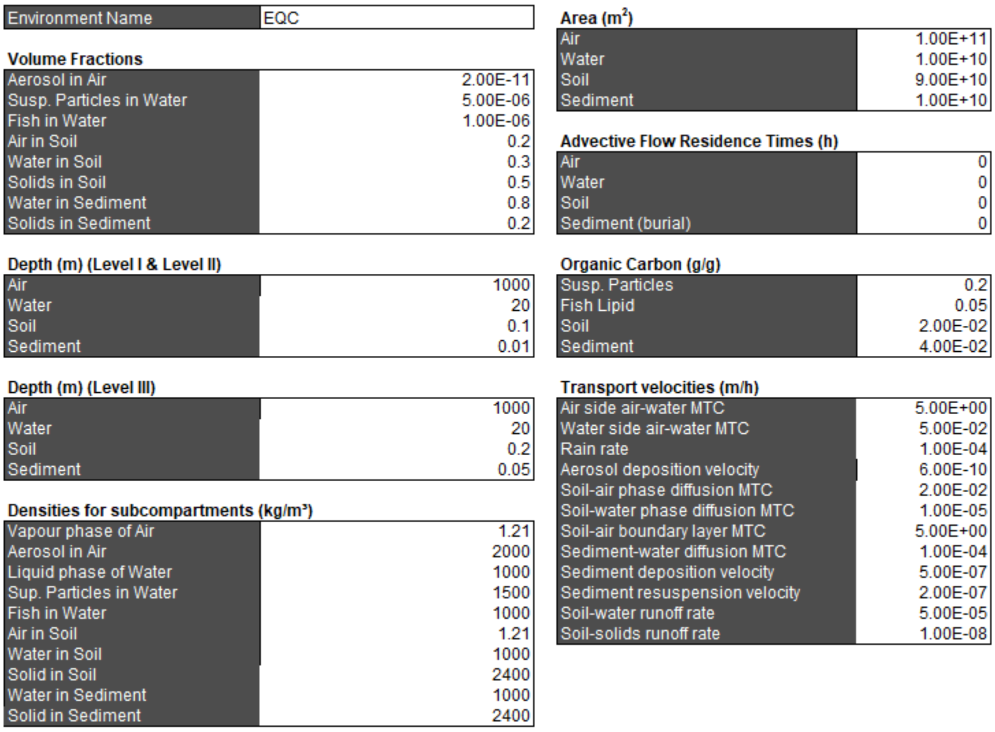
$$J_4 = D_{12} + \frac{D_{32} D_{13}}{D_{T3}}$$

3.2.1 Input Data

Necessary inputs are physicochemical properties of the query compounds, environmental parameters, and emission scenarios.

3.2.1.1 Environmental Inputs

Environmental parameters are volume fractions of subcompartments to the main compartments, densities for subcompartments, depth and area of the media, organic carbon content, and transport velocities for intermedia transport processes. Default values that were suggested by the EQC model developers were preferred in this study. The only change was to remove advective flow residence time. A screenshot of environmental inputs for the modified EQC model is demonstrated in Figure 3.1.



Environment Name	EQC

Volume Fractions

Aerosol in Air	2.00E-11
Susp. Particles in Water	5.00E-06
Fish in Water	1.00E-06
Air in Soil	0.2
Water in Soil	0.3
Solids in Soil	0.5
Water in Sediment	0.8
Solids in Sediment	0.2

Depth (m) (Level I & Level II)

Air	1000
Water	20
Soil	0.1
Sediment	0.01

Depth (m) (Level III)

Air	1000
Water	20
Soil	0.2
Sediment	0.05

Densities for subcompartments (kg/m^3)

Vapour phase of Air	1.21
Aerosol in Air	2000
Liquid phase of Water	1000
Sup. Particles in Water	1500
Fish in Water	1000
Air in Soil	1.21
Water in Soil	1000
Solid in Soil	2400
Water in Sediment	1000
Solid in Sediment	2400

Area (m^2)

Air	1.00E+11
Water	1.00E+10
Soil	9.00E+10
Sediment	1.00E+10

Advective Flow Residence Times (h)

Air	0
Water	0
Soil	0
Sediment (burial)	0

Organic Carbon (g/g)

Susp. Particles	0.2
Fish Lipid	0.05
Soil	2.00E-02
Sediment	4.00E-02

Transport velocities (m/h)

Air side air-water MTC	5.00E+00
Water side air-water MTC	5.00E-02
Rain rate	1.00E-04
Aerosol deposition velocity	6.00E-10
Soil-air phase diffusion MTC	2.00E-02
Soil-water phase diffusion MTC	1.00E-05
Soil-air boundary layer MTC	5.00E+00
Sediment-water diffusion MTC	1.00E-04
Sediment deposition velocity	5.00E-07
Sediment resuspension velocity	2.00E-07
Soil-water runoff rate	5.00E-05
Soil-solids runoff rate	1.00E-08

Figure 3.1. Environmental parameters for the modified EQC model in this study.

3.2.1.2 Physicochemical Property Inputs

Physicochemical properties, namely molar mass, temperature, melting point, vapor pressure, solubility in water, Henry's law constant (K_H), logarithm of octanol-water partition coefficient ($\log K_{ow}$), organic carbon water partition coefficient (K_{oc}) and half-lives in air, water, soil, and sediment were compiled. In the case of compilation, experimental values were prioritized.

The most important input data for the EQC model is physicochemical property information. While such data for priority pollutants are widely available, this may not always be the case for the TPs. If there are experimental data regarding physicochemical properties, then those were preferred, if not then they were estimated. However, there could be multiple experimental values for a physicochemical property. In such a case, selected values by Mackay et al. (2006) and Mackay (2001) were preferred. In the case of no selected value, the newest experimental values were taken. Physicochemical property inputs of few parent compounds and many TPs were supplied from EPI Suite^{TM} v4.11, June 2017 that was downloaded from https://www.epa.gov/tsca-screening-tools/download-epi-suitetm-estimation-program-interface-v411.

To predict physicochemical properties by using EPI Suite, SMILES notation was preferred. To obtain SMILES notation, ACD/ChemSketch (Freeware version) 2017 2.1 was used for all chemicals. Also, all degradation pathways were drawn by using ACD/ChemSketch.

In either case (EPI Suite predicted or experimental physicochemical properties), a thermodynamic consistency check is performed for all before being used in the model. All estimated or experimental data regarding priority pollutants and their TPs are presented in tabular form in Appendix A- Table A1.

The U.S. Environmental Protection Agency's EPI Suite^{TM} v4.11 was used to predict melting point, vapor pressure, solubility in water, Henry's law constant, half-live in air, water, soil, and sediment, logarithm of octanol-water partitioning coefficient ($\log K_{ow}$), and organic carbon partition coefficient (K_{oc}) at 25 °C.

Melting point and vapor pressure were estimated by EPI Suite's MPBPWIN v1.44. Weighted or mean value of the adapted Joback group contribution method (Joback, 1984) and Gold & Ogle prediction (Lyman, 1985) was taken for the melting point.

Modified Grain method (Lyman, 1985) was preferred for vapor pressure prediction because of its superiority over other prediction methods. Water solubility and K_{ow} were estimated by WATERNT v1.01 and KOWWIN v1.68, respectively. Both subprograms are based on the atom/fragment contribution method (Meylan & Howard, 1995). A chemical is converted into several fragments, then multiplication of each fragment, and its coefficient is summed. HENRYWIN v3.20 with the bond method (Hine & Mookerjee, 1975) was applied for K_H prediction. Like fragmentation, the compound is separated into individual bonds excluding some functional groups. Multiplication of each bond with a unique variable is combined in a linear equation to obtain Henry's law constant. Half-life in water was determined by BIOWIN 3 that is based on a survey with experts (Boethling et al., 1994). BIOWIN 3 result was converted to half-life in water medium by the EPI Suite. As stated in the literature (Fenner et al., 2009), half-life in water was multiplied with two and nine to obtain half-life in soil and sediment, respectively. For half-life in the air medium, AOPWIN was utilized. K_{oc} values were compiled from KOCWIN v2.00 with molecular connectivity index (Meylan et al., 1992).

All parent compounds studied were assumed not to dissociate into its ion. Ionizable characteristics of parent compounds and their TPs were determined by Chemicalize which is a web-based QSAR model. Microspecies distribution versus pH graph was plotted by this QSAR. Then the dominant form of the compound was selected considering the general pH of the environment (i.e. between 6 - 8). Describing the fate of chemicals that are capable of interconversion, such as the case for the undissociated and dissociated ion, the model to be used to describe the fate becomes more complex (Mackay et al., 1996b). Gasser et al. (2007) evaluates the fate of ionizable compounds and describes a process for adjustment of K_{oc} values. There are no other adjustments explained. So even though it was preferred not to include ionizable parent compounds as a part of this study, there were a few ionizable TPs. These were namely, Alachlor ESA, MEHP, PA, TCP, desethyl-chlorfenvinphos. They were not eliminated from the list but handled as described by Gasser et al. (2007). After supplying essential inputs, as stated in Gasser et al. (2007) few adjustments were done for the K_{oc} value of TPs. First of all, experimental K_{oc} value for TPs was preferred if possible. Secondly, consistency adjustment was applied to attain consistent predicted K_{oc} values for TPs according to Gasser and colleagues (2007).

According to Gasser et al. (2007), there are three adjustment strategies for K_{oc}. However, only two of these three methods were used, since ionizable parent compounds were excluded at the beginning. For non-ionizable compounds, the K_{oc} value of the TPs could be calculated by adding minor difference that is between predicted K_{oc} value of the TP and its parent compound to the experimental K_{oc} value of the parent compound. For ionizable compounds from the neutral parent compound, the correction factors were applied to KOCWIN v2.00 predictions. 0.5 and 0.1 would be correction factors if pKa value is around 7 and it is less than 6, respectively (Gasser et al., 2007). In case of no information about the experimental K_{oc} of the parent compound, KOCWIN v2.00 estimates without adjustment were considered.

3.2.1.3 Mode of Entry

Another necessary input of the EQC model is the emission amount into the selected media. Selected priority chemical list includes agrochemicals, solvents, and/or industrial chemicals. Under different emission scenarios, a default value (1000 kg/h) was taken for every parent compound. A fraction of formation (ff^{xy}) of each TP was multiplied with the parent compound emission rate (1000 kg/h) to find the emission amount for each TPs. Environmental amounts for selected compounds in all environmental compartments were calculated by regarding emission to only air, water, soil, and all three media.

Sensitivity analysis was done for emission into only soil medium except for trichloromethane and hexachlorobutadiene. The soil was selected because agrochemical usage in soil medium and field application of wastewater sludge that contains industrial chemicals cause a significant amount of chemical discharge to the soil. On the other hand, environmental mass distribution, PP, SP & JP calculations, FAV versus EPI Suite prediction comparison table, and sensitivity analysis of trichloromethane and hexachlorobutadiene were done considering emission into only air medium because of their high volatile characteristic.

The Fraction of Formation Determination

Degraded parent compound does not disappear from the system, but it is turned into its TPs completely or partially. Hence, the degradation of parent compounds constitutes a source for their TPs in mass balance equations. Modeling fate of TPs necessitates an additional input as compared to fate modeling of only the parent compound. This term is called the fraction of formation (ff^{xy}) symbolizing fraction of parent compound (x) that is converted into transformation product y (Fenner et al., 2009). To determine the fraction of formation (ff^{xy}) for each transformation product, three ways were utilized in this study. The first way was to take directly stated ff^{xy} values in the articles. However, finding a kinetic study that directly states ff^{xy} value is rare.

The second strategy was to obtain empirical ff^{xy} values from a kinetic study if the study has enough information for the fraction of formation calculation. By assuming first-order kinetics as stated in the literature (Fenner et al., 2000), the degradation rate constant of a parent compound and transformation product could be combined in a mathematical equation. The left side of the Equation (3.22) has a time term that shows elapsed time between the start of a parent compound degradation and the time when the maximum concentration of transformation product y is reached (Fenner et al., 2009).

$$t_{max}^{y} = \frac{\ln k^{x} - \ln k^{y}}{k^{x} - k^{y}} \tag{3.22}$$

t_{max}^{y}: Time elapsed between the start of a degradation study and the time when the maximal concentration of transformation product y is reached (hr)

k^{x}: Degradation rate constant of parent x (1/hr)

k^y: Degradation rate constant of transformation product y (1/hr)

The fraction of formation from parent compound x to transformation product y can be calculated by the following equation (Fenner et al., 2009).

$$\mathrm{ff}^{xy} = \frac{C_{max}^{y}}{C_0^x \times \left(\frac{k^x}{k^y}\right)^{\frac{k^y}{k^y - k^x}}} \qquad (3.\,23)$$

ff^{xy}: Fraction of formation from parent compound x to transformation product y

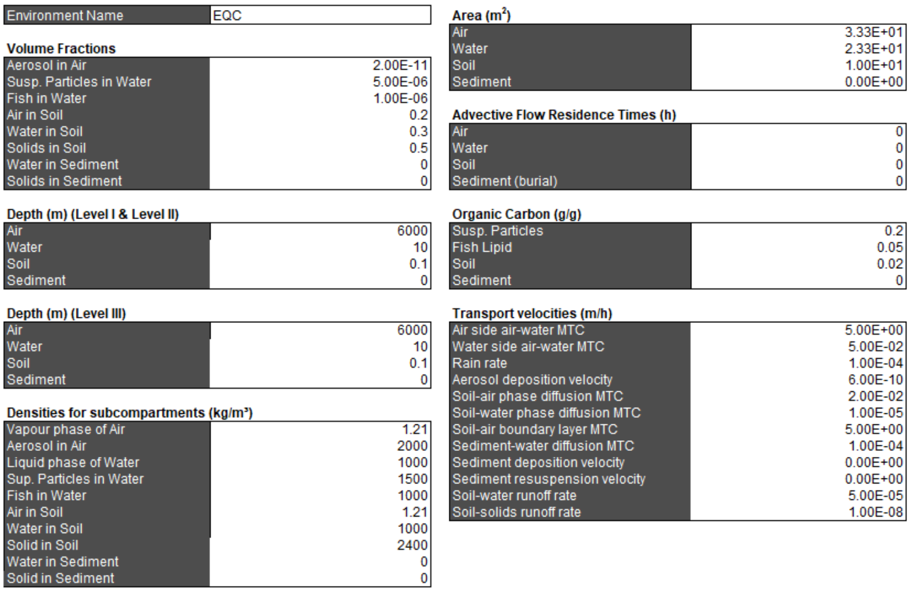
C_{max}^{y}: The maximum concentration of transformation product y (µM)

C_0^x: The initial concentration of parent compound x (µM)

Equation 3.22 was solved numerically, and then Equation 3.23 was solved. To solve both equations, MATLAB R2017b (Version 9.3), Sep 2017 was used. The last method is to utilize generic ff^{xy} values as proposed by (Fenner et al., 2009). The fraction of formation could be determined as 1, 0.5, 0.33 for single, two, and three TPs, respectively. Additionally, these ff^{xy} values were decreased by 20% to ensure the existence of the ignored minor TPs. 10% or 20% reduction was suggested for taking into account minor TPs that are not explicitly considered in the system (Fenner et al., 2009). The aforementioned three methods were used in this study for ff^{xy} determination.

3.2.2 Verification Study

Prior to the evaluation of chemicals and their TPs using the EQC model, a verification study was conducted using the chemical atrazine and its identified TPs. It is aimed to present verification of the applied methodology followed in this study. The paper by Gasser et al. (2007) was used as a reference for this purpose. Within Gasser et al's (2007) study, the primary persistence of atrazine, secondary persistence of its three TPs, and their joint persistence were calculated by modifying the Level III EQC multimedia model. For the verification study, the same exact modeling conditions were used. For this purpose, advection and sediment medium was eliminated as was done by Gasser et al. (2007). Similarly, default inputs for depths and areas of media in the EQC model were changed by considering depth values in (Fenner et al., 2000) and phase volumes in (Scheringer, 1996). Other default environmental properties were not modified. Figure 3.2 shows a screenshot of environmental inputs for the EQC model input parameters, as used in the verification study.



Environment Name	EQC

Volume Fractions

Aerosol in Air	2.00E-11
Susp. Particles in Water	5.00E-06
Fish in Water	1.00E-06
Air in Soil	0.2
Water in Soil	0.3
Solids in Soil	0.5
Water in Sediment	0
Solids in Sediment	0

Depth (m) (Level I & Level II)

Air	6000
Water	10
Soil	0.1
Sediment	0

Depth (m) (Level III)

Air	6000
Water	10
Soil	0.1
Sediment	0

Densities for subcompartments (kg/m³)

Vapour phase of Air	1.21
Aerosol in Air	2000
Liquid phase of Water	1000
Sup. Particles in Water	1500
Fish in Water	1000
Air in Soil	1.21
Water in Soil	1000
Solid in Soil	2400
Water in Sediment	0
Solid in Sediment	0

Area (m²)

Air	3.33E+01
Water	2.33E+01
Soil	1.00E+01
Sediment	0.00E+00

Advective Flow Residence Times (h)

Air	0
Water	0
Soil	0
Sediment (burial)	0

Organic Carbon (g/g)

Susp. Particles	0.2
Fish Lipid	0.05
Soil	0.02
Sediment	0

Transport velocities (m/h)

Air side air-water MTC	5.00E+00
Water side air-water MTC	5.00E-02
Rain rate	1.00E-04
Aerosol deposition velocity	6.00E-10
Soil-air phase diffusion MTC	2.00E-02
Soil-water phase diffusion MTC	1.00E-05
Soil-air boundary layer MTC	5.00E+00
Sediment-water diffusion MTC	1.00E-04
Sediment deposition velocity	0.00E+00
Sediment resuspension velocity	0.00E+00
Soil-water runoff rate	5.00E-05
Soil-solids runoff rate	1.00E-08

Figure 3.2. Environmental inputs for the modified EQC model in the verification study.

Additionally, the EQC model necessitates the physicochemical properties of the compounds and emission data. Physicochemical properties were retrieved from Gasser et al. (2007) as much as possible in order to keep any external factors impacting the results. Remaining necessary input data were retrieved from (Mackay, 2001; Fenner et al., 2003; Zelm, 2010) and EPISuite^{TM} v4.11. Physicochemical property inputs are presented with their references in Table 3.3, Table 3.4, and Table 3.5.

Table 3.3. Molar mass, melting point, vapor pressure, and solubility of atrazine and its TPs at temperature 25 °C.

Chem	Molar Mass	Melting Point	Reference	Vap. Pres (Pa)	Reference	Solubility (g/m^3)	Reference
atrazine	215	176.00	van Zelm,2010	4.00E-05	Mackay,2001	3.30E+01	van Zelm,2010
DEA	187	114.22	EPI Suite	1.24E-02	van Zelm,2010	3.20E+03	van Zelm,2010
DIA	173	103.10	van Zelm,2010	7.73E-02	van Zelm,2010	7.16E+03	van Zelm,2010
HA	197	133.90	van Zelm,2010	1.13E-03	van Zelm,2010	5.90E+00	van Zelm,2010

Table 3.4. Partitioning coefficients for atrazine and its TPs.

Chem	K_H	Reference	$\log K_{OW}$	Reference	K_{OC}	Reference
atrazine	3.61E-04	Fenner,2003	2.75	Mackay,2001	129	van Zelm,2010
DEA	1.55E-04	EPI Suite	1.78	EPI Suite	56	van Zelm,2010
DIA	1.18E-04	Fenner,2003	1.36	EPI Suite	61	van Zelm,2010
HA	6.36E-08	Fenner,2003	2.09	EPI Suite	793	van Zelm,2010

Table 3.5. Half-lives in air, water, soil, and sediment medium of atrazine and its TPs.

Chem Name	$t_{1/2,a}$ (h)*	$t_{1/2,w}$ (h)*	$t_{1/2,s}$ (h)*	$t_{1/2,sed}$ (h)**
atrazine	4.56E+00	5.52E+03	8.14E+02	1.30E+04
DEA	1.03E+01	7.20E+03	7.99E+02	1.30E+04
DIA	2.14E+01	7.20E+03	7.73E+02	1.30E+04
HA	6.96E+00	7.20E+03	2.12E+03	8.10E+03

*Gasser et al., 2007 ** EPI Suite

The emission scenario was selected identical to the one of Gasser et al. (2007) such that the default amount of 1000 kg/hour of atrazine was emitted to surface soil at 90% and to air 10%. For TPs, emission data were determined regarding the fraction of formation concept, as explained below.

All transformation mechanisms were assumed that they were first-order kinetics as it is stated in the literature (Fenner et al., 2000). Half-life in various environmental compartments was retrieved from Gasser and colleagues (2007). Then, the degradation rate constants of TPs were calculated by using Equation (3.24).

$$\frac{0.693}{t_{1/2}} = k \tag{3. 24}$$

Atrazine initial concentration (C_0^x) was stated in the kinetic study that was conducted by Torrents and colleagues (1997). The maximum concentration of each TPs (C_{max}^y) were directly read from the figures that were plotted by Torrents and colleagues (1997). Then, fraction of formation (ff^{xy}) values for each TP was calculated according to Fenner et al. (2009) and given in Equation (3.23).

The maximum concentration of HA that was labeled as OIET in Figure 3.3 was approximately taken as 3.5 and 4 μM to calculate the persistence of HA under two different initial conditions. Maximum concentrations of DEA (in other words CIAT) and DIA (in other words CEAT) were approximately read as 5.5 and 3 μM from Figure 3.4, respectively. These are indicated with blue lines on the figures.

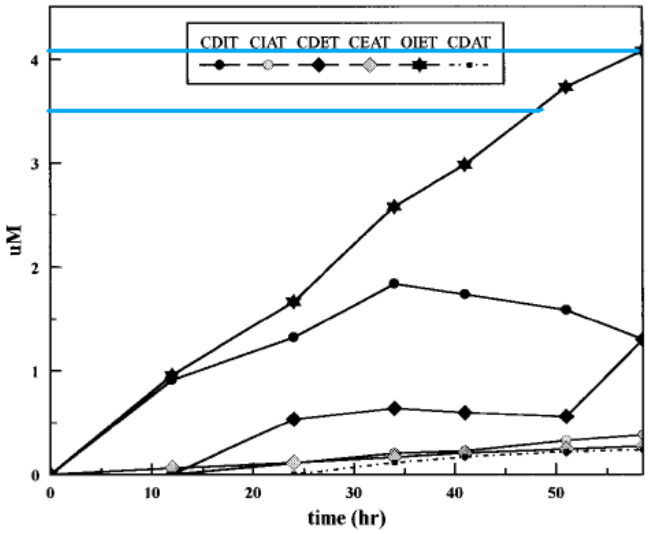


Figure 3.3. TPs of direct photolysis of 30 μM atrazine (Torrents et al., 1997). Blue lines show approximately read chemical concentrations.

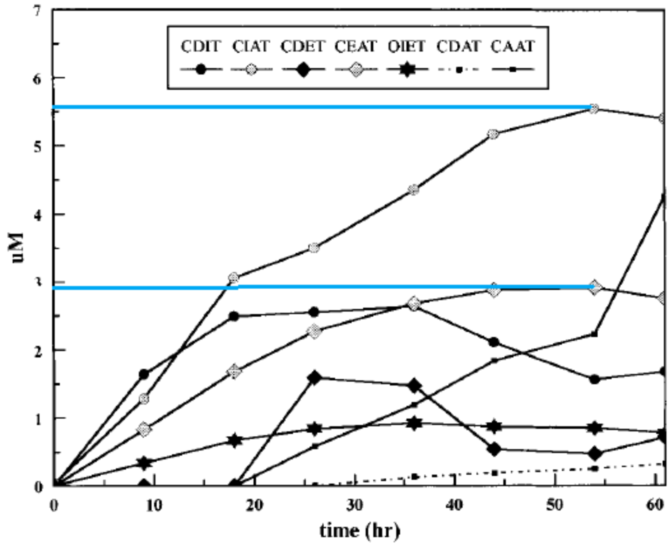


Figure 3.4. TPs of indirect photolysis of 30 μM atrazine (Torrents et al., 1997). Blue lines show approximately read chemical concentrations.

3.2.3 Sensitivity Study

After advection processes were eliminated from the EQC model, it was used for the sensitivity analysis of atrazine. This subchapter aims to select the best increment amount for sensitivity analysis for all compounds. It was assumed that the selected increment would be applicable for all compounds. In this case, the default amount of 1,000 kg/h atrazine was emitted into the soil. Since atrazine is an agrochemical and it is likely to be used in the soil compartment. The total amount in the environment was directly taken from the EQC model. Then, persistence was calculated dividing this mass term to the total emission rate. Percentage difference was determined to subtract base case (i.e. inputs without any change) to changed case and then divided by the changed case (Webster et al., 1998).

Compilation of total mass amount and persistence calculation for atrazine was done in case each physicochemical input was increased as 0.1%, 1%, and 10%, separately. For example, the melting point of atrazine was increased as 0.1% and other inputs were kept as they were. Later, the environmental mass was taken from the Level III EQC model, and persistence was calculated by Equation (3.37). Similar to the melting point, each input was increased by 0.1%, 1% or 10% while keeping other inputs the same. This procedure was repeated just changing the increment amount. While conducting sensitivity analysis, thermodynamic consistency check was not performed, because such an attempt would prevent only one parameter from changing and convoluting the resulting change persistence.

3.3 Thermodynamic Consistency Check of Physicochemical Properties Input Into the EQC Model

Thermodynamic consistency refers to internally consistent interrelated physicochemical property data e.g. vapor pressure, solubility, and Henry’s Law Constant. Regardless of the origin of such data, they are generally not fully consistent (Beyer et al., 2002). However, internally consistent data is needed for model calculations. To do this, Beyer and colleagues proposed an adjustment procedure to take advantage of all available physicochemical properties regarding thermodynamic constraints (Beyer et al., 2002). Therefore, in this study, an analytical adjustment procedure to obtain a consistent input dataset for the EQC model was preferred.

First of all, all LDVs were converted to units of mol/m^3 or dimensionless partition coefficients.

$$\mathrm{logK_{aw}} = \mathrm{H/RT} \tag{3. 25}$$

R is the gas constant 8.314 J/ (mol×K)

T is the absolute temperature (K)

The vapor pressure was transformed into solubility in the air by the equation (Cole & Mackay, 2000).

$$\mathrm{S_A} = \mathrm{P^s/RT} \tag{3. 26}$$

$\mathrm{P^s}$: vapor pressure

Secondly, LDV were placed into equations that indicate the theoretical relationship between related inputs. There is a relationship between the air-water partitioning coefficient and solubility in air and water. The aim is to obtain zero after placing LDV into the equation (3.27).

$$\mathrm{logK_{aw}} - \mathrm{logS_A} + \mathrm{logS_w} = 0 \tag{3. 27}$$

Placing LDV could generate deviation (ε) from the ideal case. The result of the equation was equal to ε. Lastly, by assuming three physicochemical properties (i.e. K_{aw}, $S_{A,}$ and S_w) contribute equally to the deviation, so they were changed as the adjusted term (δ) that can be calculated from as ε/3.

$$(\mathrm{logK_{aw}} - \delta) - (\mathrm{logS_A} + \delta) + (\mathrm{logS_w} - \delta) = 0 \tag{3. 28}$$

Hence, LDVs turn into adjusted values after manipulation with δ.

A similar methodology can be applied for partitioning between air, water, and octanol phases. Two different equations were applicable regarding $\log K_{ow}$ value. These equations were obtained from (Beyer et al., 2002). As a first step, LDVs for $\log K_{ow}$, $\log K_{oa}$, and $\log K_{aw}$ were placed one of the equations that are stated in Equation (3.29) and Equation (3.30).

$$\log K_{ow} - 0.117 - \log K_{oa} - \log K_{aw} = 0 \quad \text{for } \log K_{ow} \leq 4 \tag{3. 29}$$

$$1.35\log K_{ow} - 1.58 - \log K_{oa} - \log K_{aw} = 0 \quad \text{for } \log K_{ow} > 4 \tag{3.30}$$

Deviation (ε) and adjustment term ($\delta = \varepsilon/3$) were calculated. The adjustment term was subtracted from each term in the equation. According to our understanding, coefficient (1.35) of $\log K_{ow}$ could affect $\log K_{ow}$ adjustment. Therefore, one more adjustment term (δ_2) was calculated if $\log K_{ow}$ of a compound was higher than 4.

$$(1.35\log K_{ow} - 1.58 - \delta) - (\log K_{oa} + \delta) - (\log K_{aw} + \delta) = 0 \tag{3.31}$$

$$(1.35\log K_{ow} - 1.58 - \delta) = 1.35(\log K_{ow} - \delta_2) - 1.58 \tag{3.32}$$

As an example, K_{ow} adjustment for polychlorinated biphenyl (PCB) 15 is presented below.

$$(1.35\log K_{ow} - 1.58 - 0.0198) = 1.35(\log K_{ow} - \delta_2) - 1.58 \tag{3.33}$$

$$\delta_2 = 0.0147 \tag{3.34}$$

$$10^{(logK_{ow}-\delta_2)} = 10^{5.23-0.0147} = 1.64 \times 10^5 \qquad (3.35)$$

The obtained corrected result (1.64×10^5) was close to (1.61×10^5) that was stated final adjusted K_{ow} for PCB 15 in the article (Beyer et al., 2002). It should be noted that for many of the TPs, no experimental physicochemical data is available, therefore for most TPs, all properties are estimated by EPI Suite. The aforementioned thermodynamic consistency check and consequent adjustment procedure were applied for all.

There are cases where the final adjusted value has more than an order of magnitude difference between the original one. An overall summary of the range of numeric value of adjustment terms is presented in Table 3.6. Since there is no other option but to predict and then input thermodynamically consistent data into the EQC model, and even though this procedure is conducted to reduce any errors, prediction of properties, as well as these adjustments, are considered as another source of uncertainty that contributes to the uncertainty of persistency evaluations.

Table 3.6. Median and Range values for adjustment terms for vapor pressure, solubility, $K_{H,}$ and K_{ow}.

Data Source of Physicochemical Input	**Median**	**Range**
Vapor Pressure		
LDV	-0.002	From -0.880 to 0.04
EPI Suite Prediction	-0.072	From -1.98 to 1.7
Solubility		
LDV	-0.002	From -0.88 to 0.04
EPI Suite Prediction	-0.072	From -1.98 to 1.7
Henry’s Law Constant		
LDV	-0.002	From -0.88 to 0.04
EPI Suite Prediction	-0.072	From -1.98 to 1.7

Table 3.6. (Cont'd).

Data Source of Physicochemical Input	**Median**	**Range**
Octanol-Water Partition Coefficient		
LDV	-0.061 for delta -0.004 for delta2	From -0.381 to 0.345 for delta, From -0.798 to 0.173 for delta2
EPI Suite Prediction	-0.039 for delta, 0.009 for delta2	From -0.255 to 0.395 for delta, From -0.065 to 0.958 for delta2

3.4 Evaluation of EQC Model Results

P_{ov} is the residence time of a chemical in a closed system. It is the ratio between total chemical mass present in the system to the total emission into the system (Webster et al., 1998).

$$P_{ov} = \frac{\sum M_{jT}}{\sum E_j} \qquad (3.36)$$

P_{ov}: Overall Persistence (h)

M_{jT}: The total amount of a compound in a compartment (j shows a compartment) (kg)

E_j: Emission rate into a compartment (kg/h)

To assess the effects of TPs, the P_{ov} concept was extended by introducing PP and JP. While PP indicates the persistence of only parent compound (Fenner et al., 2000), JP refers to the persistence of the parent compound including the persistence of its TPs (Fenner et al., 2003).

$$\mathrm{PP} = \frac{\mathrm{M}_{\mathrm{PC}}^{\mathrm{ss}}}{\mathrm{S}_{\mathrm{PC}}} \qquad (3.37)$$

$$\mathrm{JP} = \frac{\mathrm{M}_{\mathrm{PC}}^{\mathrm{ss}} + \sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{M}_{\mathrm{i}}^{\mathrm{ss}}}{\mathrm{S}_{\mathrm{PC}}} = \mathrm{PP} + \sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{CTP}_{\mathrm{i}} \qquad (3.38)$$

PP: Primary Persistence (h)

$\mathrm{M}_{\mathrm{PC}}^{\mathrm{ss}}$: Steady-state mass of a parent compound (kg)

$\mathrm{M}_{\mathrm{i}}^{\mathrm{ss}}$: Steady-state mass of a compound in all environmental compartments (i shows a transformation product) (kg)

n: Number of TPs

S_{PC}: The emission rate of the parent compound (kg/h)

$\mathrm{CTP}_{\mathrm{i}}$: Secondary persistence (contribution to persistence of TP_{i} to joint persistence) (h)

The Level III EQC model was utilized to determine $\mathrm{M}_{\mathrm{PC}}^{\mathrm{ss}}$ and $\mathrm{M}_{\mathrm{i}}^{\mathrm{ss}}$. S_{PC} value was taken 1000 kg/hour as default excluding p,p’-DDT. It was 18 kg/h for p,p’-DDT, since it comes from impurity in dicofol (Qiu et al., 2005).

Hence, the primary persistence of the parent compounds, secondary persistence of each TPs, and joint persistence were calculated. Each substance family (i.e. parent compound + its all TPs) is represented in a graph with the P_{ov} threshold value that was suggested by Webster et al. (1998).

Additionally, various emissions scenarios were applied for parent and TP fate modeling to understand the effects of mode-of-entry on predicted environmental mass in different media. Environmental mass in all environmental compartments under four emission scenarios are compiled in the graph for each chemical family.

Furthermore, the accumulation of each member in a family was evaluated considering all environmental compartments. The members are compared with each other. Also, possible intermedia transport mechanisms were regarded by evaluating the environmental mass distribution of the chemicals under various emission scenarios.

CHAPTER 4

RESULTS AND DISCUSSION

The effect of TPs on the overall persistency of selected priority pollutants are evaluated under three sub-sections in this chapter. Firstly, preliminary studies undertaken on the EQC model, such as model verification, sensitivity analysis as well as a comparison between levels of the EQC model are presented in Chapter 4.1. Then, each selected priority pollutant is evaluated using the EQC model and results are presented each in a sub-section starting Chapter 4.2. Degradation pathway schemes, compiled inputs and environmental mass distributions and persistency of substance families are explained in the subsections 4.2 through 4.15. An overall comparative evaluation of results is discussed in the last subchapter, namely Chapter 4.16.

4.1 Preliminary Studies on the EQC Model

First of all, a verification study was conducted using atrazine. Later, the results of Level I, II, and III of the EQC model were compiled for atrazine. Additionally, the effect of selecting different increments for sensitivity analysis was analyzed and results are presented.

4.1.1 EQC Model Verification Study with Atrazine

Gasser et al. (2007) evaluated the impact of TPs on the persistence of a number of pesticides, including atrazine, by estimating their environmental persistence via including both parent and its TPs. They used two multimedia models, one of which was a three-box model. In our study, before applying the EQC model, which can also be considered a box model, on the selected priority pollutants, we carried out studies on atrazine and its TPs for verification of a number of steps for using the EQC model, including the calculation of the indicator, JP.

The first step for the calculation of JP is the identification of TPs associated with the parent compound. In the case of atrazine, Gasser et al. (2007) identified 6-amino-2-chloro-4-isopropylamino-s-triazine (DEA), 6-amino-2-chloro-4-ethylamino-s-triazine (DIA), 4-ethylamino-6-isopropylamino-2-hydroxy-s-triazine (HA) as the major TPs of atrazine. The degradation pathway indicating the main TPs for atrazine is shown in Figure 4.1. The verification study was carried out with these four compounds.

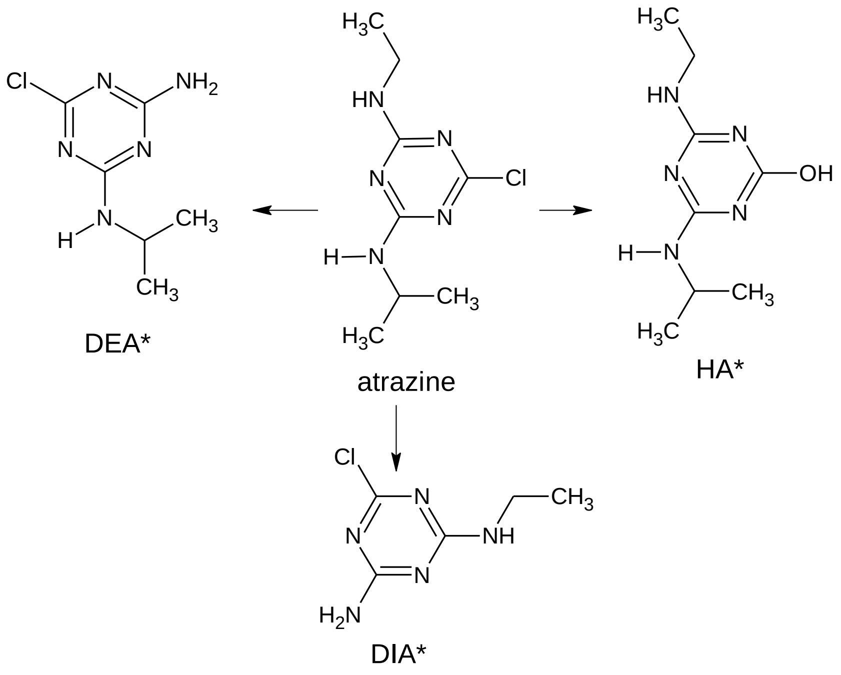


Figure 4.1. Degradation scheme of atrazine (Gasser et al., 2007*).

The second step is to determine the fraction of formation ff^{xy} for each TP. This metric gives the fraction of the parent compound, x that is converted into the transformation product, y (Fenner et al., 2009). The ff^{xy} values were calculated for each TP of atrazine are presented in Table 4.1.

Table 4.1. The calculated fraction of formation values in the soil for DEA, DIA, and HA.

Chemical	**Calculated ff^{xy} values in soil**
DEA[1]	0.503
DIA[1]	0.279
HA[2]	0.212* or 0.242**

*If C_{max}^{HA} is read as 3.5 μM from Figure 3.3 of (Torrents et al., 1997). ** $C_{max}^{HA} = 4\ \mu M$, 1: from indirect photolysis, 2: from direct photolysis

The next step is to evaluate atrazine and its TPs using the EQC model so that primary persistence (i.e. persistence of the parent compound) and secondary persistence (i.e. persistence of the TP) is determined. For this purpose, in order to conduct a comparative study to one of Gasser et al. (2007), we adopted a similar three-box model composed of air, water and soil media, specifications of which are given in Table 4.2.

Table 4.2. The evaluative environment used in the EQC model for verification study.

Media	**Depth (m)** (Fenner et al., 2000)	**Phase volume (m^3)** (Scheringer, 1996)
Air	6000	2×10^5
Water	10	233
Soil	0.1	1

The primary and secondary persistence, as well as the calculated joint persistence values (in terms of hours) are given in Table 4.3 and Figure 4.2. The ratio between joint persistence and primary persistence is 3.02 or 3.08 depending on which initial HA concentration was used. As explained in Materials and Methods, some values are read from graphs provided in papers, therefore some variation is possible during determination of ff^{xy}. For this reason, two different fraction of formation values were calculated for HA (as presented in Table 4.1). As can be seen in Table 4.3, the primary persistence of atrazine as obtained in our study and that of Gasser et al. (2007) are very close to each other. The difference in secondary persistence of TPs could be due to use of different physicochemical property data. Although inputs in this study were compiled from Gasser et al. (2007) as much as possible, some inputs had to be retrieved from other studies because they were not reported. For further information about inputs, Table 3.3, Table 3.4, and Table 3.5 could be seen. Although secondary persistence values show some variation, overall, the JP/PP ratio obtained in our study is around 3.0 where it is reported as 2.5 in Gasser et al. (2007).

Table 4.3. Comparison of persistence values in this study and those from Gasser et al. (2007).

Chemical	**Persistence Type**	**Persistence (h)*** (This study)	**Persistence (h)**** (This study)	**Persistence (h)** (Gasser et al., 2007)
Atrazine	**Primary Persistence**	**2220**	**2220**	**2023**
DEA	Secondary Persistence	2230	2230	1248
DIA	Secondary Persistence	1300	1300	552
HA	Secondary Persistence	944	1080	1270
	Joint Persistence	**6698**	**6832**	**5093**
	Q ratio (JP/PP)	**3.02**	**3.08**	**2.5**

*Taking $C_{max}^{HA} = 3.5\ \mu M$ **Taking $C_{max}^{HA} = 4\ \mu M$

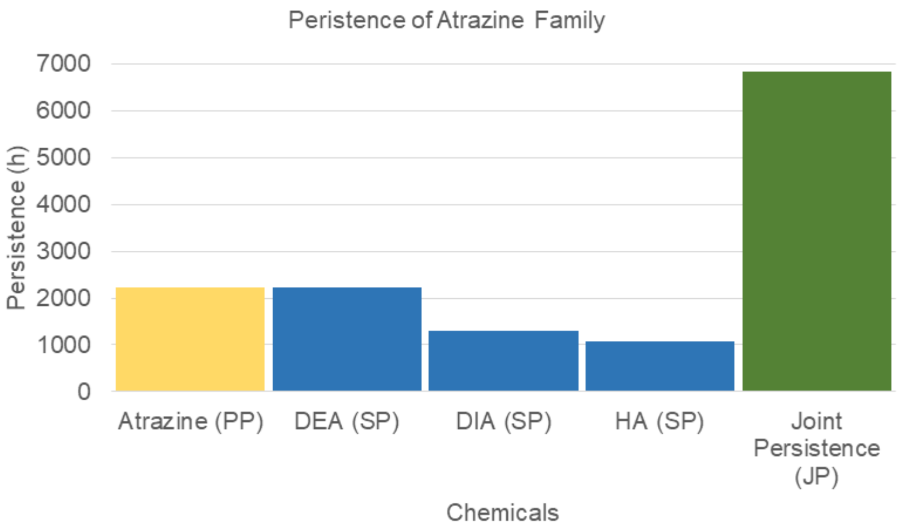


Figure 4.2. Results of persistence evaluation for atrazine family when $C_{max}^{HA} = 4\ \mu M$.

Additionally, differences between SP of TPs are higher. Even though the 3-box multimedia model is mimicked in the EQC Level III model, a fraction of formation values were not reported in Gasser et al.'s (2007) study. Hence, the maximum concentration of each TP and initial concentration of atrazine were retrieved from Torrents et al. (1997) that was found from the literature for verification study. Gasser and coworkers (2007) could have used other kinetics data to calculate fractions of formation. Considering the potential variation in physicochemical property information as well as degradation half-lives and fraction of formation values, it was decided that the JP/PP value calculated in our study and that of Gasser et al. (2007) were close to each other, and verification study was satisfactory.

4.1.2 Sensitivity Analysis

Inputs required by the EQC model were explained in detail in the Materials and Methods Chapter. Accordingly, in order to run the EQC model, input is required regarding the physicochemical properties of the compound (i.e. molar mass, temperature, melting point, vapor pressure, solubility in water, Henry's Law Constant, reaction half-life in air, in water, in soil, and in sediment, log K_{ow}, K_{oc}), environment (i.e. volume fractions, depths, areas, densities for subcompartments, organic carbon content, and transport velocities), mode-of-entry and emission amount.

The impact of each physicochemical input parameter on the output of the model was tested via a sensitivity study. For this purpose, each parameter was changed by 0.1%, 1%, and 10% of its original value, individually, and the effects of this incremental change on the persistence calculation was observed. The main purpose here is to decide on a percentage in which a noticeable difference could be observed in the persistence value. Table 4.4 shows the output of the Level III EQC model for the three tested incremental changes in each physicochemical parameter. For example, the first line of Table 4.4 could be explained as: if the melting point of atrazine is increased by 0.1%, 1%, or 10% of its original value, its environmental concentration and persistence is increased by 37.57%. The EQC model calculates fugacity of a compound in each phase, and then the environmental mass of compound in each phase as well as the total amount for the compound in the evaluative environment. If the total amount or persistence of the compound does not change as a result of these calculations, then it means that the model is not sensitive to this parameter. However, for some physicochemical inputs, the output can change due to a change in the physicochemical input regardless of the increment amount. These point to sensitive parameters or processes for which any change results in a change of the output of the model.

Table 4.4. A total mole of the atrazine in the environment, persistence, and percentage difference.

Modified Input*	**Increment Amount**								
	0.10%			**1%**			**10%**		
	Total Amount (mole)	**Persistence (d)**	**Percent Diff. (%)**	**Total Amount(mole)**	**Persistence (d)**	**Percent Diff. (%)**	**Total Amount (mole)**	**Persistence (d)**	**Percent Diff. (%)**
atrazmelt	9.95E+06	89.40	37.57	9.95E+06	89.40	37.57	9.95E+06	89.40	37.57
atrazvap	6.21E+06	55.81	0.00	6.21E+06	55.81	0.00	6.21E+06	55.81	0.00
atrazsol	9.95E+06	89.40	37.57	9.95E+06	89.40	37.57	9.95E+06	89.40	37.57
atrazhenry	9.95E+06	89.40	37.57	9.95E+06	89.40	37.57	9.95E+06	89.39	37.56
atrazair	9.95E+06	89.40	37.57	9.95E+06	89.40	37.57	9.95E+06	89.40	37.57
atrazwater	9.95E+06	89.40	37.57	9.95E+06	89.46	37.61	1.00E+07	90.01	37.99
atrazsoil	9.95E+06	89.47	37.62	1.00E+07	90.12	38.07	1.07E+07	96.55	42.19
atrazsed	9.95E+06	89.40	37.57	9.95E+06	89.40	37.57	9.95E+06	89.40	37.57
atrazow	9.95E+06	89.40	37.57	9.95E+06	89.40	37.57	9.95E+06	89.40	37.57
atrazorgca	9.95E+06	89.41	37.57	9.96E+06	89.49	37.63	1.00E+07	90.26	38.17
Atrazine (base case)	**6.21E+06**	**55.81**							

*atrazmelt=melting point, atrazvap=vapor pressure, atrazsol=water solubility, atrazhenry=Henry's law constant, atrazair=half-life in air, atrazwater=half-life in water, atrazsoil=half-life in soil, atrazsed=half-life in sediment, atrazow=octanol-water partitioning coefficient, atrazorgca=organic carbon partitioning coefficient

The change in a physicochemical input can disrupt its relationship between other inputs. For example, an increase in solubility could cause a decreasing effect on volatility, so this compound is more likely to stay in the water. If the reaction in water is slower, higher persistence for this compound would be determined. However, after the threshold (0.1% for atrazsol), the relationship between solubility and vapor pressure cannot be disrupted up to a point. For instance, when solubility is increased like 100%, a decrease in persistence can be detected as long as persistence value is denoted by seven significant figures.

It was observed that an incremental change of 0.1% or 1% had a similar effect on persistence, and that changes in 10% were more noticeable. Therefore, a 10% incremental increase was selected. This can be understood by comparing the persistence difference in the case of half-life in water, soil, or organic carbon partitioning coefficient is increased by three increments. Therefore, 10% was selected as the incremental change percentage to be applied for all compounds

4.1.3 Level I, II, III Demonstration Results

As explained in Chapter 2, the EQC model runs in three different levels (Mackay et al., 1996c):

- Level I: steady-state, equilibrium, closed system, no degradation
- Level II: steady-state, equilibrium with degradation and advection
- Level III: steady-state, non-equilibrium with degradation, advection and intermedia transfer.

Typically, Level III, being the most realistic, is the one frequently used in the literature. In this study, Level III is used, but advection is eliminated in all trials so that merely mass losses due to the degradation processes are considered. As Mackay et al. (1996c) also emphasize, the residence time of a chemical depends on degradation and advection. While from a global viewpoint, persistence due to reaction is the most relevant, from a local viewpoint, both reactive and advective processes are important. In this study, since there is a global concern regarding priority pollutants, rather than a local one, the advection term was kept at zero during all model runs.

Figure 4.3 shows what would happen to the emission of 100,000 kg atrazine into the evaluative environment of the EQC model Level I. The result of Level I indicates 18% and 82% of atrazine end up in soil and water, respectively. Atrazine amount in air and sediment media was negligible as compared to other media. From these results, we can comment that the very little amount of atrazine in the air medium indicates that its LRTP is low.

Figure 4.4 shows what would happen to the emission of 1,000 kg/h atrazine into the evaluative environment of the EQC model Level II. The output indicates that the main loss mechanisms are reaction in water, followed by reaction in soil. The level I and II results propose that atrazine in the water compartment should be a concern. This output also points to the importance of realistic degradation rate information for atrazine in water and soil media.

Figure 4.5 shows the EQC model Level III output for atrazine after 1,000 kg/h emission into only air medium. Level III enables compounds to be introduced into different compartments, and since it presents results for non-equilibrium & steady-state conditions, the choice of emission medium does make a difference in the intermedia mass transfer of the compound as well as its P_{ov}.

Similar to Figure 4.5, Figure 4.6 demonstrates atrazine distribution in Level III, but this time, 1,000 kg/h atrazine was emitted to only water medium, rather than air. Figure 4.7 indicates 1,000 kg/h atrazine distribution in the same evaluative environment in Figure 4.5 and Figure 4.6, however, atrazine was emitted into only soil medium. Lastly, Figure 4.8 shows atrazine distribution when 1,000 kg/h atrazine emission was emitted each to air, water, and soil, media.

Emission into different media was assessed to understand the mode-of-entry effect. Mode-of-entry means input rates of chemical into a medium (Hughes et al., 2012). A user has to decide on mode-of-entry, i.e. from which medium the chemical should be introduced into the environment. This typically shows the use pattern of a chemical (Hughes et al., 2012), such as a pesticide being applied onto soil, but also enables the user to compare the impact of emitting a chemical into one medium or another.

Figure 4.5 indicates 56% and 44% of atrazine in soil and water, respectively. Residence time for advection seems very high, this is because advection is eliminated from the model. In addition, air-soil and air-water partitioning are seen to likely happen, as indicated by the high intermedia transport (i.e. 900 kg/h and 100 kg/h) from air to these media. Run-off from soil to water (i.e. 604 kg/h) could be a significant contributor to a high atrazine amount in water.

When 1000 kg/h atrazine is emitted into the water like in Figure 4.6, the highest mass of atrazine is observed in water (99.8%) with a minor amount in sediment. The primary loss mechanisms are reaction in water, followed by degradation in sediment. In addition, there is a net transfer to sediment as 0.56 kg/h, of which almost all of it (0.556 kg/h) is lost in sediment reactions.

When 1000 kg/h atrazine is emitted into soil Figure 4.7, the highest mass of atrazine is in soil medium (i.e. 60.2 %) and then water (i.e. 39.8%). It is interesting to note that a great change in % mass distribution of atrazine is observed when compared to emission into water. The primary loss mechanism is degradation in water followed by degradation in soil. Also, intermedia transport from soil to water is a significant mechanism.

When atrazine is input into the evaluative environment from all three phases (i.e. air, water, and soil at 1000 kg/h each), major portions of atrazine, i.e., 45% and 55% end up in soil and water, respectively, with negligible amounts in the sediment. There is deposition from air to soil and water. Like emission into soil scenario, the primary loss mechanism is the reaction in water followed by reaction in soil.

To conclude, the equilibrium distribution of atrazine yields 82% water and 18% soil, however, non-equilibrium distribution yields quite different proportions depending on the mode-of-entry. The primary loss mechanism is the reaction in the water phase, followed by the reaction in soil. In addition, intermedia transfer between soil and water phases seem to be important and can increase the mobility of atrazine.

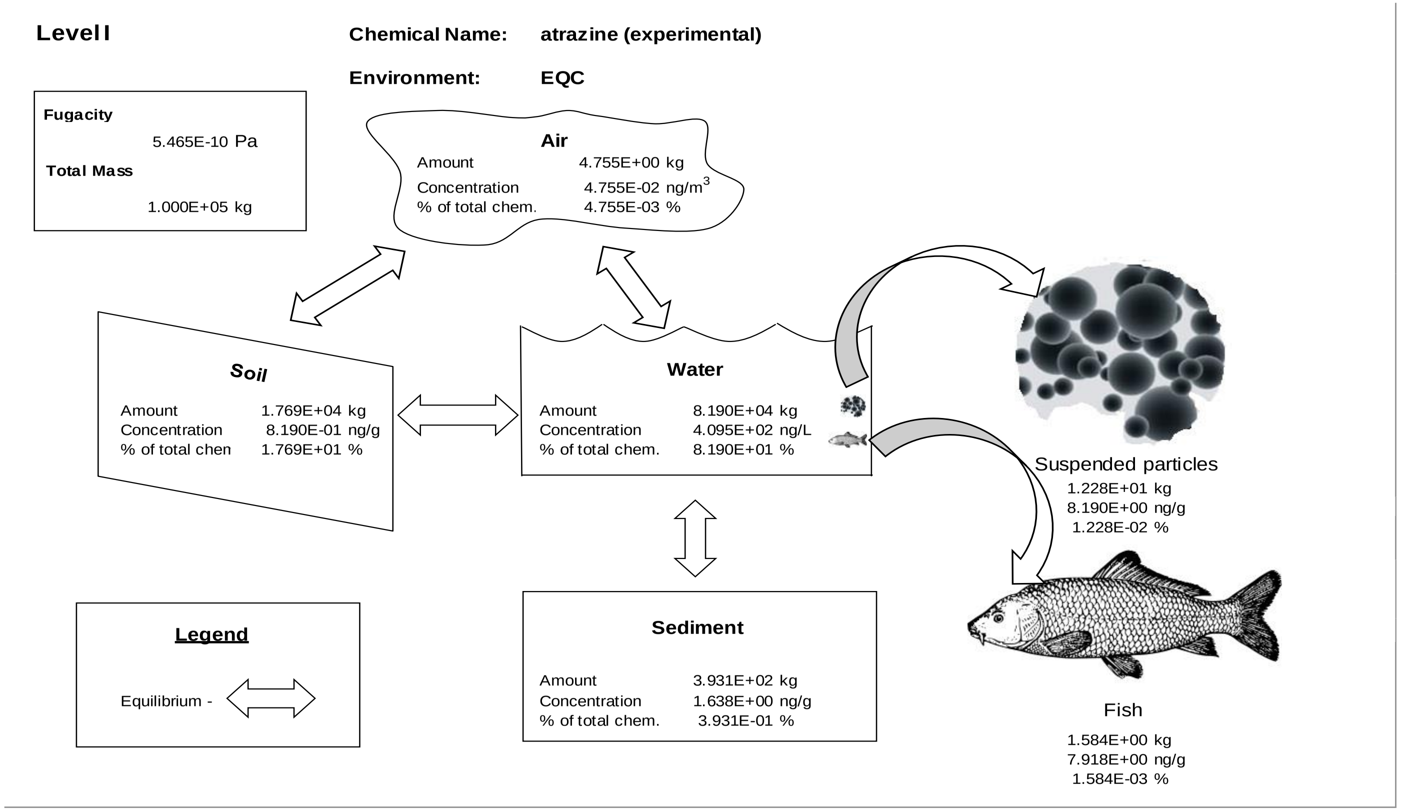


Figure 4.3. EQC Model: Level I for atrazine

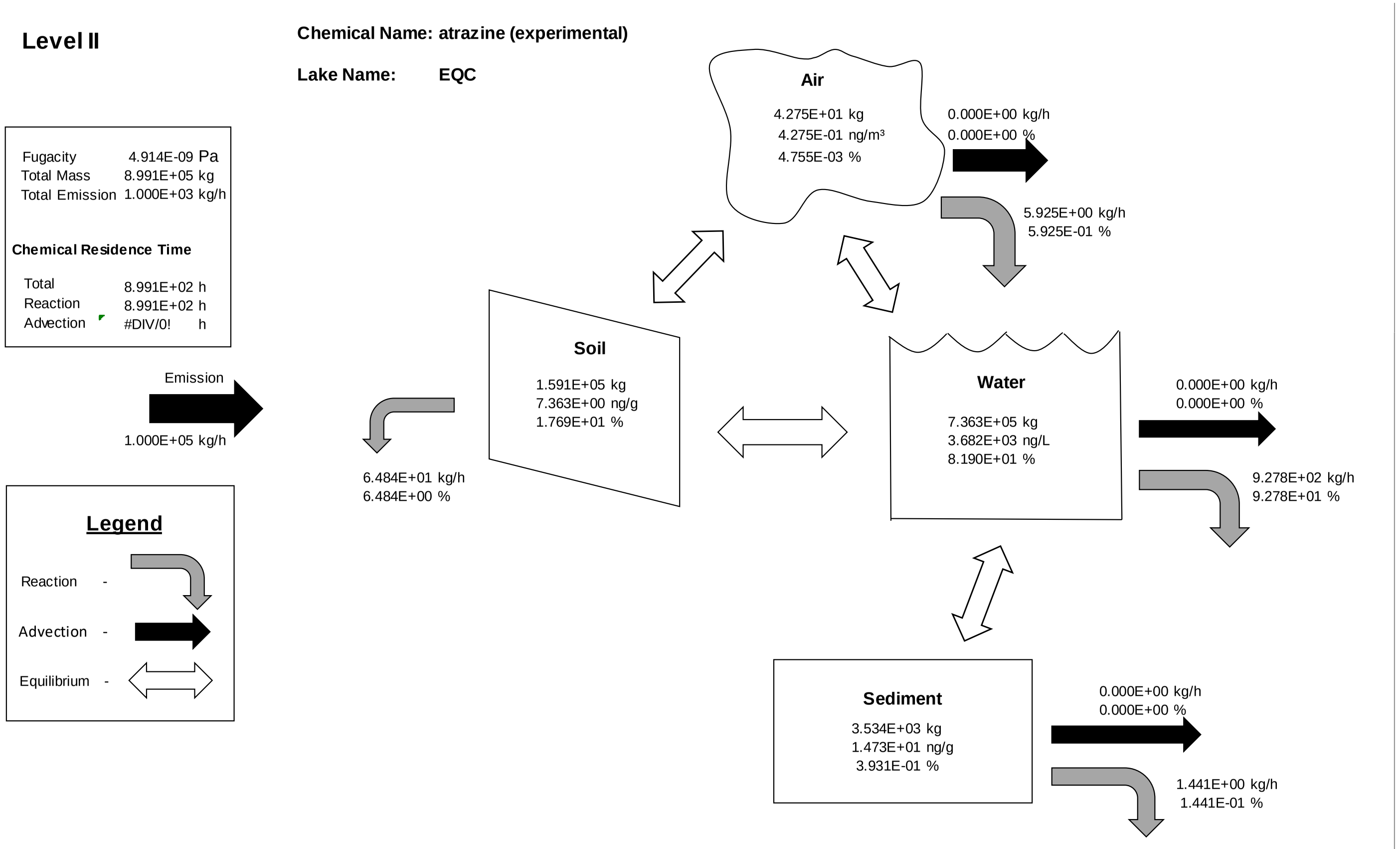


Figure 4.4. EQC Model: Level II results for atrazine.

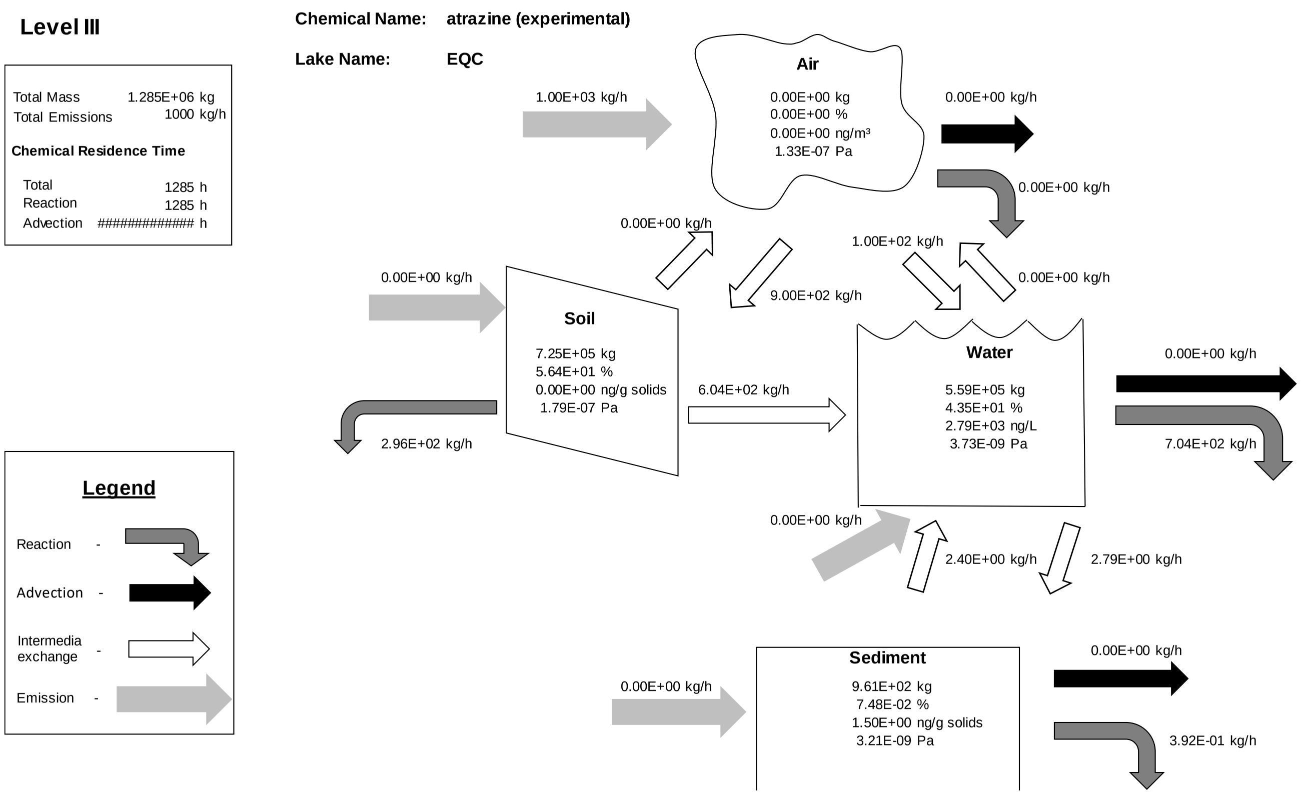


Figure 4.5. EQC Model: Level III results for 100% emission of atrazine to air.

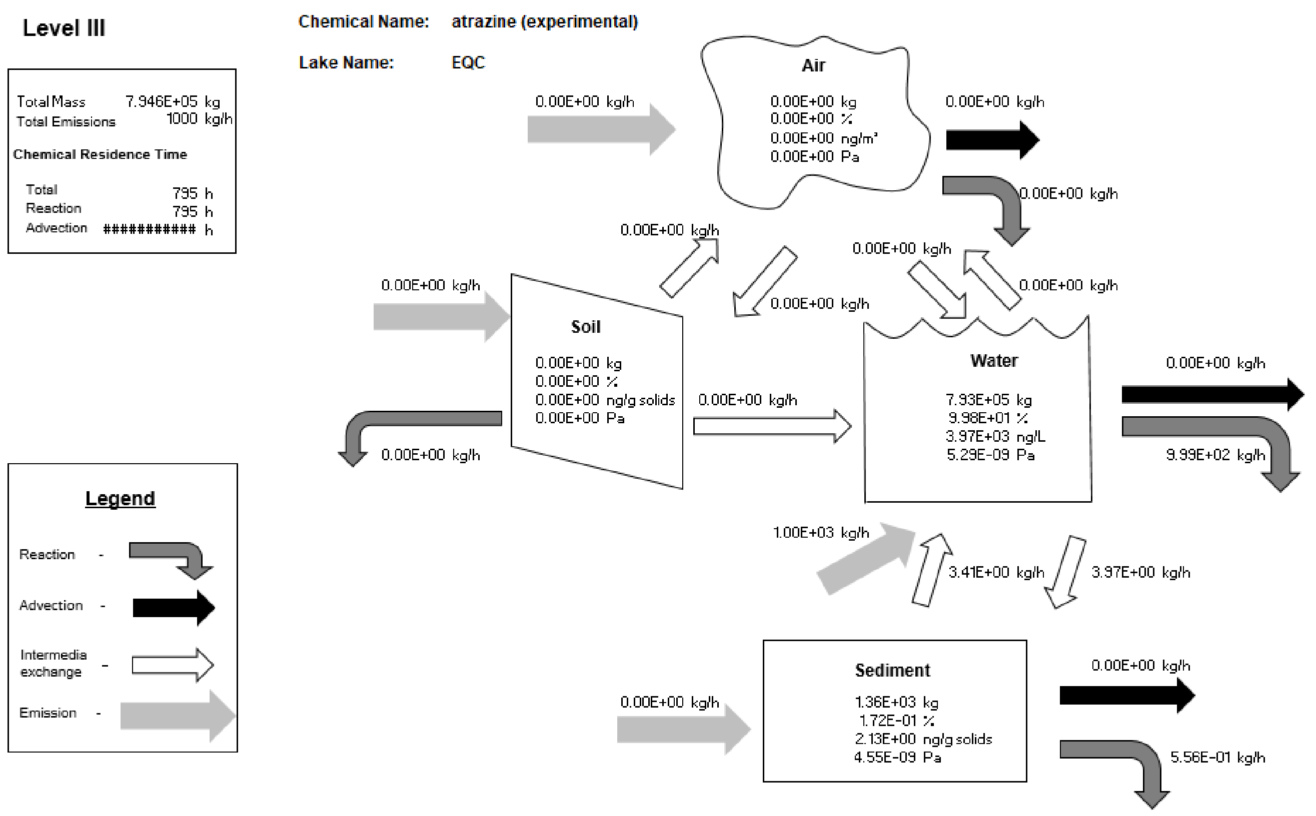


Figure 4.6. EQC Model: Level III results for 100% emission to water.

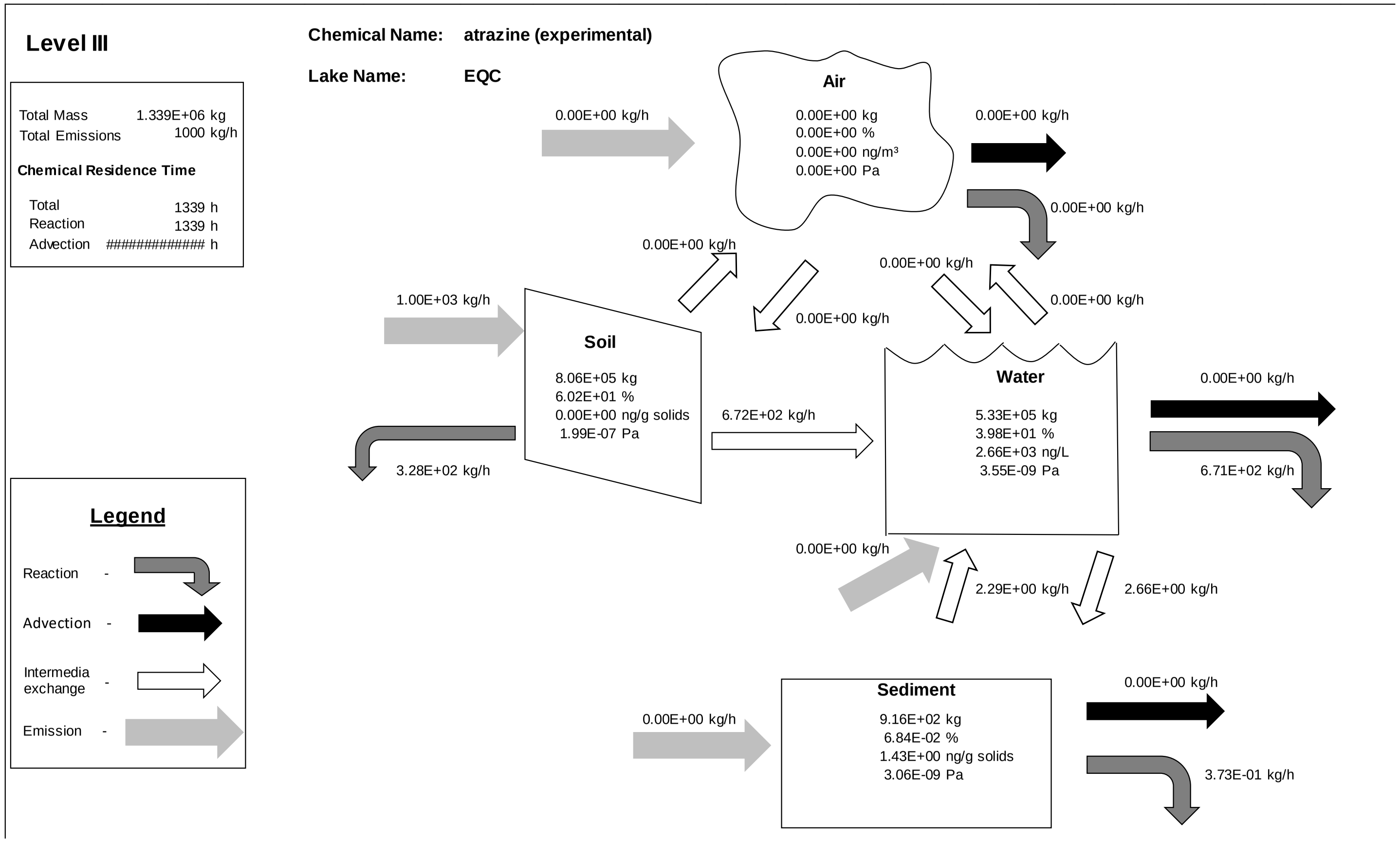


Figure 4.7. EQC Model: Level III results for 100% emission to soil.

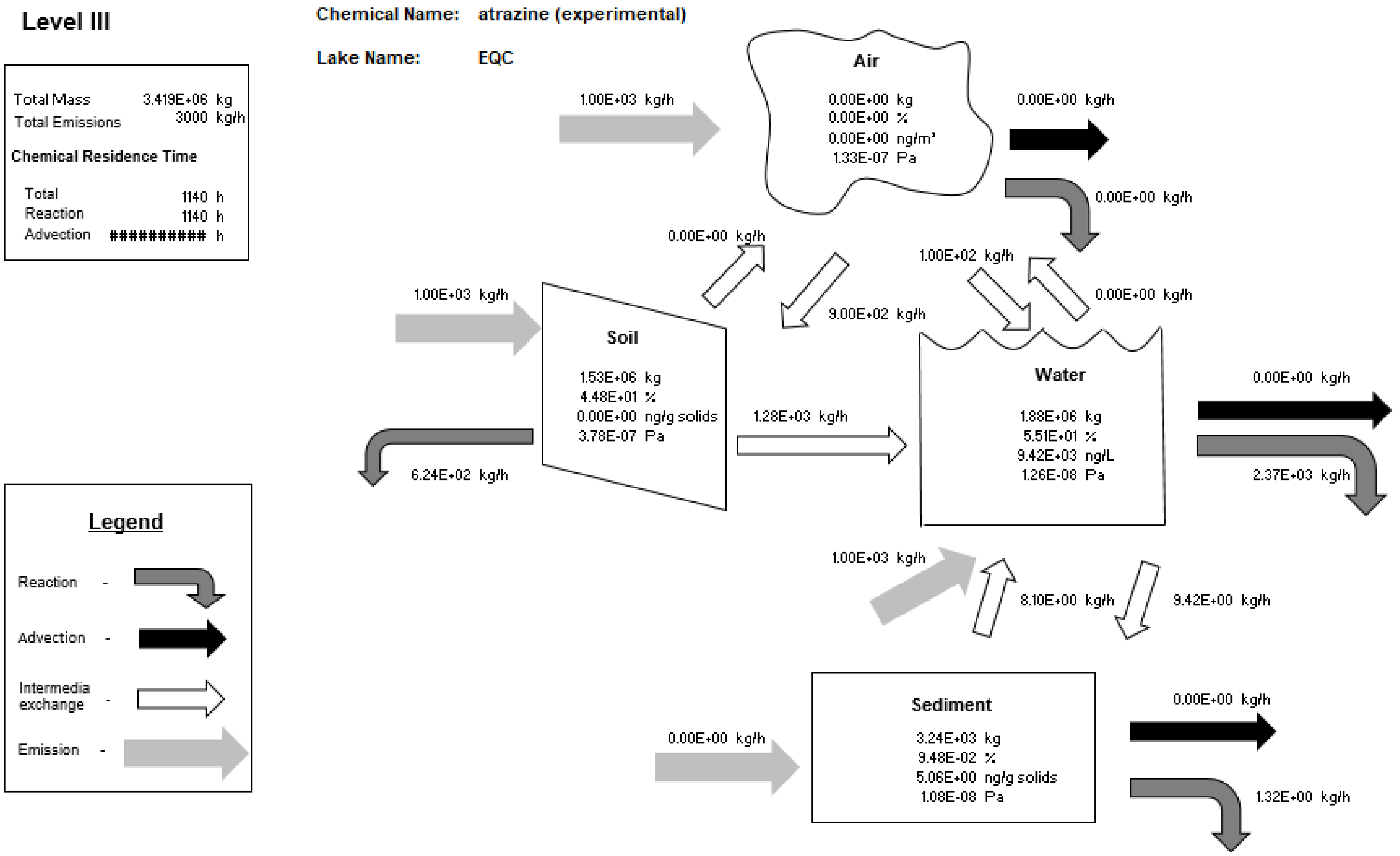


Figure 4.8. EQC Model Level III results for emission to air, water, and soil media.

4.2 Atrazine

Atrazine is an efficient and durable herbicide that is frequently applied in maize fields (Ju et al., 2020). Because of its inhibitory effects on photosynthesis, atrazine has been commonly used since 1958 (Jones & Winchell, 1984). Although it was banned in Europe, some countries are still using it for agricultural purposes (Hertfordshire, 2020). In addition to its effectiveness as a herbicide, atrazine was shown to be an endocrine disruptor interfering with the functions of several hormones (Song et al., 2014). Therefore, many studies focus on the environmental fate of atrazine (Torrents et al., 1997).

4.2.1 Degradation Pathway Scheme for Atrazine

The main atrazine degradation pathway is presented in Figure 4.9. According to this figure, there are three main TPs associated with atrazine, namely, DEA, DIA, and HA. These products can be formed as a result of a number of different mechanisms. Firstly, all three could be formed via biological and abiotic degradation mechanisms in soil, surface water, and/or groundwater (Thomas et al., 1994). Secondly, when atrazine gets excited through direct photolysis, dechlorination, and hydroxylation reactions occur, upon which HA is produced (Torrents et al., 1997). DEA and DIA on the other hand, are a result of chlorodealkylation of atrazine after indirect photolysis (Torrents et al., 1997).

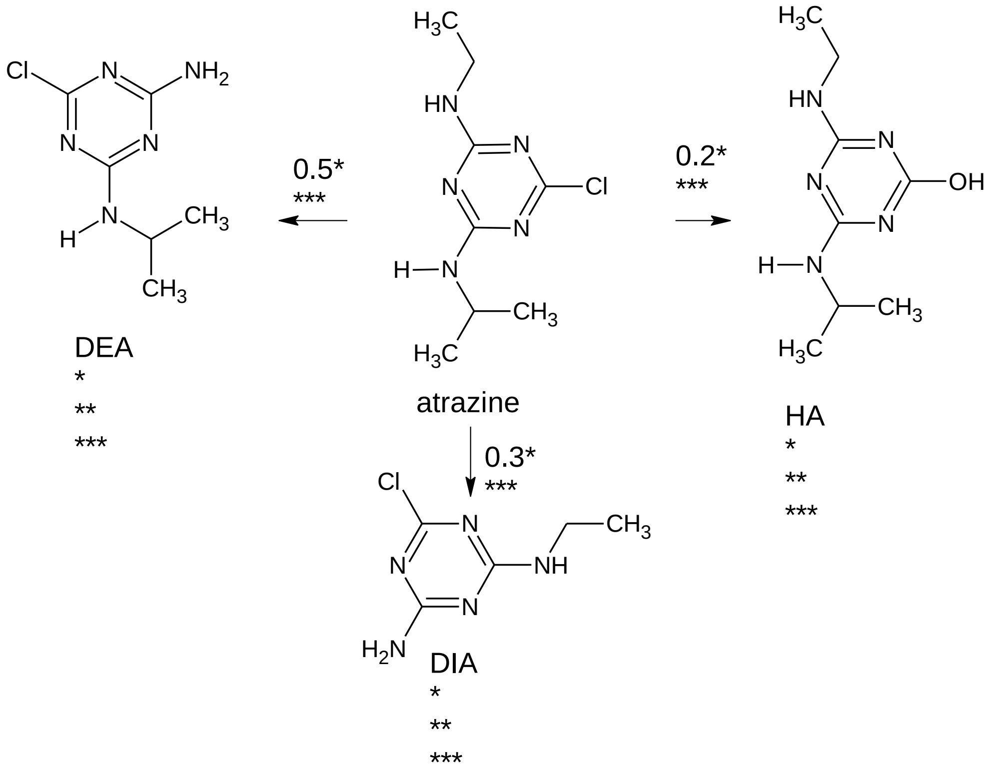


Figure 4.9. Degradation scheme of atrazine (Gasser et al., 2007*; Thomas et al., 1994**; Torrents et al., 1997***). Number on each arrow indicates the fraction of formation of TPs from the parent compound.

4.2.2 Physicochemical Properties for Atrazine Family

Compiled physicochemical property data from the literature for atrazine and estimated physicochemical properties for its TPs are presented in Appendix A-Table A1. As explained in the Material and Methods chapter, a thermodynamic consistency check was performed for experimental/estimated physicochemical properties before use in the model. These final adjusted values (FAVs) for parent chemical and their TPs are given in Appendix A- Table A2.

4.2.3 Evaluation and Persistency of Atrazine Family

Table 4.5 shows a summary of EQC model output when atrazine and each of its TPs is introduced into the evaluative environment via four different modes-of-entry: air only, water only, soil only at 1000 kg/hr each, and all three media equally, again at 1000 kg/hr each but this time at a total of 3000 kg/hr. As shown in Table 4.5, atrazine does not partition into air, and its presence in sediment medium is negligible. Atrazine ends up mainly in soil and water – depending on the mode of entry into the environment. Run-off from soil to water and deposition from air into water & soil are important intermedia transport processes, as indicated by the movement of chemical from its introduced media to that presented as % mass as an output of Level III in the table.

Table 4.5. Amount of atrazine & its TPs as kg and percent in different environmental compartments and persistence, as obtained from the EQC model.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
Atrazine	Air	0.00E+00	0	5.59E+05	43	7.25E+05	56	9.61E+02	0	1.28E+06	1285
	Water	0.00E+00	0	7.93E+05	100	0.00E+00	0	1.36E+03	0	7.95E+05	795
	Soil	0.00E+00	0	5.33E+05	40	8.06E+05	60	9.16E+02	0	1.34E+06	1339
	All three	0.00E+00	0	6.28E+05	55	5.10E+05	45	1.08E+03	0	1.14E+06	1140
DEA	Air	1.03E+03	0	4.47E+05	31	9.70E+05	68	1.93E+03	0	1.42E+06	2840
	Water	1.23E-01	0	1.04E+06	100	1.15E+02	0	4.48E+03	0	1.04E+06	2086
	Soil	8.90E+00	0	4.38E+05	27	1.20E+06	73	1.89E+03	0	1.64E+06	3280
	All three	3.47E+02	0	6.41E+05	47	7.23E+05	53	2.77E+03	0	1.37E+06	2735
DIA	Air	5.36E+02	0	3.05E+05	38	4.96E+05	62	1.06E+03	0	8.02E+05	2875
	Water	5.61E-02	0	5.79E+05	100	5.19E+01	0	2.02E+03	0	5.82E+05	2084
	Soil	4.90E+00	0	2.90E+05	33	5.78E+05	66	1.01E+03	0	8.69E+05	3116
	All three	1.80E+02	0	3.92E+05	52	3.58E+05	48	1.36E+03	0	7.51E+05	2692
HA	Air	9.64E+00	0	8.33E+04	18	3.82E+05	82	4.89E+02	0	4.66E+05	2198
	Water	7.70E-06	0	2.75E+05	99	3.05E-01	0	1.61E+03	1	2.77E+05	1305
	Soil	5.38E-04	0	6.23E+04	13	4.26E+05	87	3.65E+02	0	4.89E+05	2305
	All three	3.21E+00	0	1.40E+05	34	2.69E+05	66	8.23E+02	0	4.10E+05	1936

DEA and DIA are not likely to accumulate in air or sediment media. They distribute into water and soil, like atrazine. Similar intermedia transport processes as those affecting atrazine are significant for these TPs. For HA, the soil medium captures a major part of HA emission into air, soil, and all three scenarios. HA has a lower aqueous solubility when compared to that of DEA and DIA, so minor partitioning into sediment medium is observed. On the other hand, lower degradation half-lives of HA compared to DEA and DIA in all media results in lower persistency as can be seen in the last column of the table. Based on Table 4.5, the environmental mass of each compound was plotted with respect to various media under different emission scenarios in Figure 4.10. Blue bars of atrazine indicate atrazine distribution if 1000 kg/h is emitted into only air phase. Orange bar of atrazine demonstrates the distribution of atrazine providing that 1000 kg/h atrazine is emitted into the only water phase. Similar to the previous two cases, grey bars of atrazine show atrazine distribution due to its emission into only soil medium. However, yellow bars of atrazine show atrazine distribution if it is emitted as 3000 kg/h into air, water, and soil media equally. To compare the last scenario to others, the environmental mass of atrazine in each medium is divided into three. For TPs of atrazine, colors of bars and emission scenarios are the same as atrazine. Nonetheless, ff^{xy} was used to calculate how much TP is emitted in each scenario.

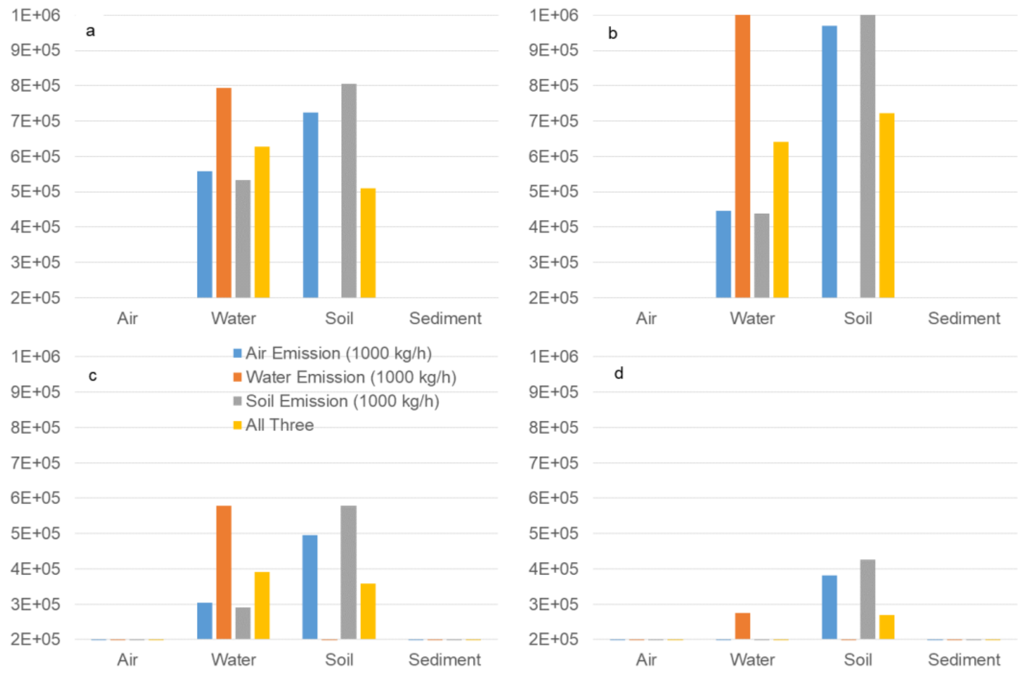


Figure 4.10. Amount (kg) of (a) atrazine, (b) DEA, (c) DIA, and (d) HA in the environment.

The persistence of each compound (parent or TP) in Table 4.5 was calculated by taking the ratio of total environmental amount of the compound to its emission rate. Primary (for atrazine) and secondary persistence (for TPs) for soil mode-of-entry from the EQC model output are used to calculate joint persistence by taking into account fraction of formation of TPs (as shown on the arrows of Figure 4.9).

Primary persistence of atrazine and secondary persistence of its TPs together with their joint persistence are presented in Figure 4.11. As can be seen from Figure 4.11, the persistence of atrazine is increased considerably if its degradation products are taken into consideration in case of soil mode-of-entry. Persistence of degradation products could be less, almost equal to or higher than the parent compound.

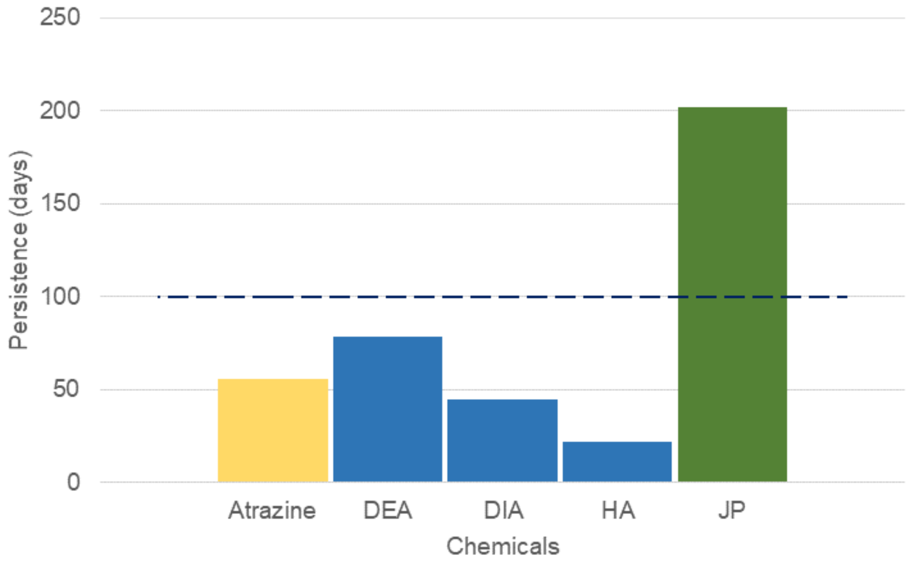


Figure 4.11. Persistence of atrazine family with P_{ov} criterion of 100 days (Webster et al., 1998).

As an example, DEA has a higher persistence contribution to joint persistence, but DIA and HA have less contribution as compared to atrazine. One reason for this is the fraction of formation, where it is 0.5 for DEA while it is 0.3 and 0.2 for DIA and HA, respectively. Mode-of-entry and partitioning effects should be considered in persistence, so strict cutoff criteria could not be applicable. Additionally, uncertainty and variability in half-lives should be included. Therefore, Webster and colleagues (1998) suggested considering the distribution of overall half-lives. According to their study, the environmental persistence criterion might be summarized as “the overall environmental persistence should be less than 100 days with a frequency of at least 50%."(Webster et al., 1998). Later, 100 days criterion was used by another study (Panagopoulos & MacLeod, 2018) to analyze the persistence of fate of cyclic and linear volatile methyl siloxanes. Hence, 100 days criterion was also used in this study. Overall, the joint persistence of the atrazine family exceeds this proposed threshold by Webster et al. (1998).

Comparison between FAV and EPI Suite prediction for physicochemical inputs and their effects on chemical amount and persistence were done for only parent compounds. The main reason is that physicochemical inputs of TPs are almost totally retrieved from EPI Suite due to a lack of experimental data.

Table 4.6 was prepared to understand the predictive capability of EPI Suite and to determine the effects of deviation in inputs on chemical amount/persistence. Abbreviations used in Table 4.6 are explained in Table 4.7.

The difference between inputs as the % column of Table 4.6 demonstrates the predictive capability of the EPI Suite. A minus sign in the difference between the input columns indicates that EPI Suite overpredicts the relevant physicochemical input. The difference between inputs was calculated as follows. Please note that there is no threshold value for the percent difference between inputs.

$$\text{Diff. Btw Inputs as } (\%) = \frac{(\text{FAV} - \text{EPI Suite prediction})}{\text{FAV}} \times 100 \qquad (4.\ 1)$$

The percentage difference between EPI Suite predicted and FAV for vapor pressure is high, and this difference generates a 38% increase in persistence and chemical concentration. The vapor pressure should be concerned more than other properties excluding half-life in the water medium.

Even though differences between FAV and EPI Suite prediction for melting point, solubility, Henry’s law constant, log K_{ow} and K_{oc} are also quite noticeable, these differences do not generate any effect on persistence.

Table 4.6 Effect of FAVs and EPI Suite predicted inputs on atrazine amount and persistence with percentage difference.

Input Data	**FAV**	**EPI Suite Value**	**Diff. Btw Inputs as (%)**	**Chem Amount (mole)**	**Persistence (d)**	**Percent Diff. Btw Outputs(%)**
atrazine				6.21E+06	56	
atrazmeltpred	1.74E+02	1.14E+02	34	6.21E+06	56	0
atrazvaporpred	4.00E-05	1.11E-03	-2675	9.95E+06	89	38
atrazsolubpred	3.00E+01	1.54E+02	-413	6.21E+06	56	0
atrazHenrypred	2.88E-04	1.55E-03	-438	6.21E+06	56	0
atrazairhalfpred	5.00E+00	9.00E+00	-80	6.21E+06	56	0
atrazwaterpred	5.50E+02	1.44E+03	-162	1.02E+07	92	39
atrazsoilpred	1.70E+03	2.88E+03	-69	7.18E+06	64	13
atrazsedpred	1.70E+03	1.30E+04	-665	6.21E+06	56	0
atrazlogKowpred	2.59E+00	2.87E+00	-11	6.21E+06	56	0
atrazKocpred	1.00E+02	2.25E+02	-125	6.21E+06	56	0
atrazpredicted				1.78E+07	160	65

Table 4.7. Explanation of abbreviated terms in Table 4.6.

Abbreviation	Meaning
atrazine	EPI Suite was not used for any inputs
atrazmeltpred	EPI Suite was only used for melting point. Other inputs are FAV.
atrazvaporpred	EPI Suite was only used for vapor pressure. Other inputs are FAV.
atrazsolubpred	EPI Suite was only used for solubility. Other inputs are FAV.
atrazHenrypred	EPI Suite was only used for Henry's law constant. Other inputs are FAV.
atrazairhalfpred	EPI Suite was only used for half-life in air. Other inputs are FAV.
atrazwaterpred	EPI Suite was only used for half-life in water. Other inputs are FAV.
atrazsoilpred	EPI Suite was only used for half-life in soil. Other inputs are FAV.
atrazsedpred	EPI Suite was only used for half-life in sediment. Other inputs are FAV.
atrazlogKowpred	EPI Suite was only used for logKow. Other inputs are FAV.
atrazKocpred	EPI Suite was only used for Koc. Other inputs are FAV.
atrazpredicted	EPI Suite was used for all inputs.

Final adjusted (i.e. applying mathematical procedure to literature derived values) and EPI Suite predicted half-life in water and soil are different from each other with 162% and 69%, respectively and such overprediction of these parameters results in an increase in persistence of 39% and 13%, respectively.

Change in half-lives in other media does not create any deviation on persistence. Overall, half-life in water, vapor pressure, and half-life in soil might be important physicochemical parameters and they should be determined correctly as much as possible.

Sensitivity analysis for the atrazine family is demonstrated in Figure 4.12 and an explanation about the y-axis is represented in Table 4.8. For example, Figure 4.12 (a) shows the percent change in primary persistence of atrazine when a single parameter is changed by 10%. This is performed one by one for each of the parameters listed in Table 4.8. Similarly, the same is conducted for TPs where this time the impact on their secondary persistence is evaluated. The sensitivity study is performed only for soil as the mode-of-entry. According to this figure, half-life in soil and half-life in water are sensitive parameters for calculation of persistence. However, change in K_{oc} value gains significance for TPs. The K_{oc} values for TPs were estimated by EPI Suite, while that of atrazine was retrieved from the literature. The K_{oc} of atrazine is an order of magnitude greater than those of TPs, which could present a reason for relative insensitivity for this parameter. An interesting, and hard to explain outcome is observed for HA when its vapor pressure is changed. A 10% increase/decrease in vapor pressure of HA surprisingly changes its persistence to the same extent; about a 35% reduction in persistence. There are a few other compounds in the coming sub-chapters where similar results are observed. An explanation for this response of the EQC model is attempted in the final overall evaluation section.

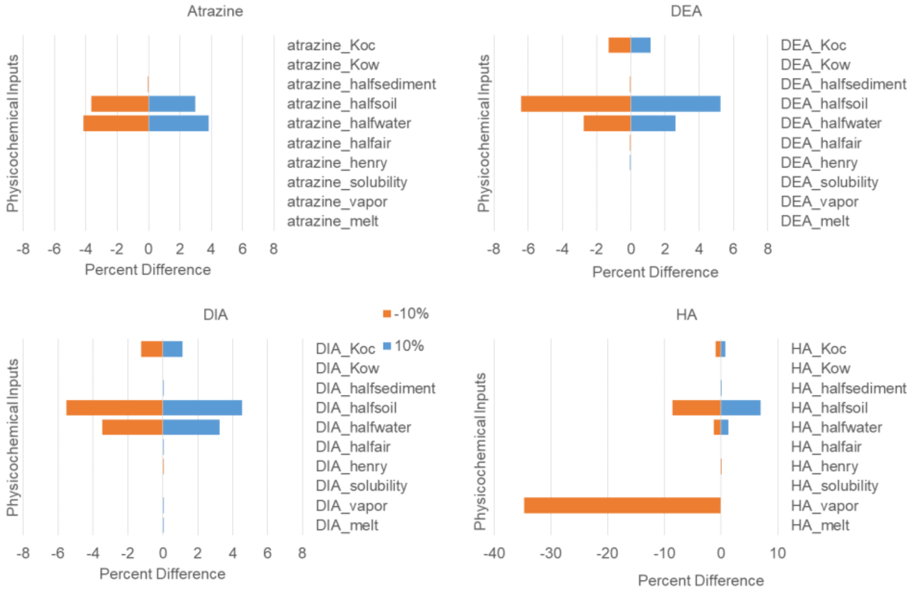


Figure 4.12. Percent difference impact on persistence upon a 10% change in physicochemical parameter values for atrazine, DEA, DIA, and HA.

Table 4.8. Explanation about Figure 4.12.

Abbreviation	Meaning
atrazine_Koc	Only Koc was decreased as 10% or increased as 10%
atrazine_Kow	Only logKow was decreased as 10% or increased as 10%
atrazine_halfsediment	Only half-life in sediment was decreased as 10% or increased as 10%
atrazine_halfsoil	Only half-life in soil was decreased as 10% or increased as 10%
atrazine_halfwater	Only half-life in water was decreased as 10% or increased as 10%
atrazine_halfair	Only half-life in air was decreased as 10% or increased as 10%
atrazine_henry	Only Henry's law constant was decreased as 10% or increased as 10%
atrazine_solubility	Only solubility was decreased as 10% or increased as 10%
atrazine_vapor	Only vapor pressure was decreased as 10% or increased as 10%
atrazine_melt	Only melting point was decreased as 10% or increased as 10%

4.3 Dicofol and DDT

Dicofol with the trade name Kelthane, is an organochlorine pesticide. It is commonly used for protecting vegetables, fruit trees, and cotton from mites (Lerche et al., 2002). Its active ingredient is 2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol (Qiu et al., 2005). In addition to molecular structure similarity between dicofol and DDT (Oliveira et al., 2012), dicofol is generally generated from technical DDT (Qiu et al., 2005). While high water solubility of dicofol allows degradation, degradation of DDT is not possible because of its low solubility. Also, dicofol has a lower environmental half-life and lower ability to accumulate in the environment when compared to DDT. Furthermore, the generation of more toxic degradation products is valid for DDT, but is deemed not to be the case for dicofol (USEPA, 1998a).

East-Southeast Asia, Mediterranean Coast, and Northern-Central America are main dicofol consumers (Debabrata & Sivakumar, 2018). Despite debatable endocrine disruption characteristic of dicofol (USEPA, 1998a), it has residual and acute toxicity in the environment (Yu et al., 2008). Although dicofol can have a reproductive influence on some species, its effect is different from the effect of DDT. Hence, the use of dicofol is justified due to posing a lesser risk than DDT (USEPA, 1998a).

4.3.1 Degradation Pathway Scheme for Dicofol and DDT

Electron transfer reactions occur on TiO_2 nanoparticles. Therefore, an active radical that reacts with dicofol can be produced by aqueous phase and products from electron transfer reactions. Active OH radicals can attack dicofol, so bis (4-chlorophenyl) methanone is generated (Yu et al., 2008).

Furthermore, efficient sonochemical treatment causes dicofol degradation. In this method, thermal decomposition with a radical attack is the main mechanism for the first TP formation. After bis (4-chlorophenyl) methanone losses chloride atom successively, 4-chlorophenyl phenyl methanone, and diphenylmethanone occur (Debabrata & Sivakumar, 2018). Figure 4.13 represents the degradation scheme of dicofol.

Relevant TPs of DDT were detected in the field to verify possible transformation pathways. P, p’-DDT is converted into p, p’-DDE under aerobic conditions, but reductively dechlorinated to p, p’-DDD in surface soils under anaerobic conditions. Both TPs can be transformed into p, p’-DDNU (Huang et al., 2018). On the other hand, visible light photosensitized DDT dehalogenation can cause p, p’-DDE, p, p’-DDD, and p, p’-DDNU formation. This photosensitized system with thermal elimination causes removal of the first chlorine atom, so p, p’-DDE forms. Then electron transfer lead of an electron leads to p, p’-DDD formation via dechlorination (Lin & Chang, 2007). Figure 4.14 represents the degradation scheme of p, p’-DDT.

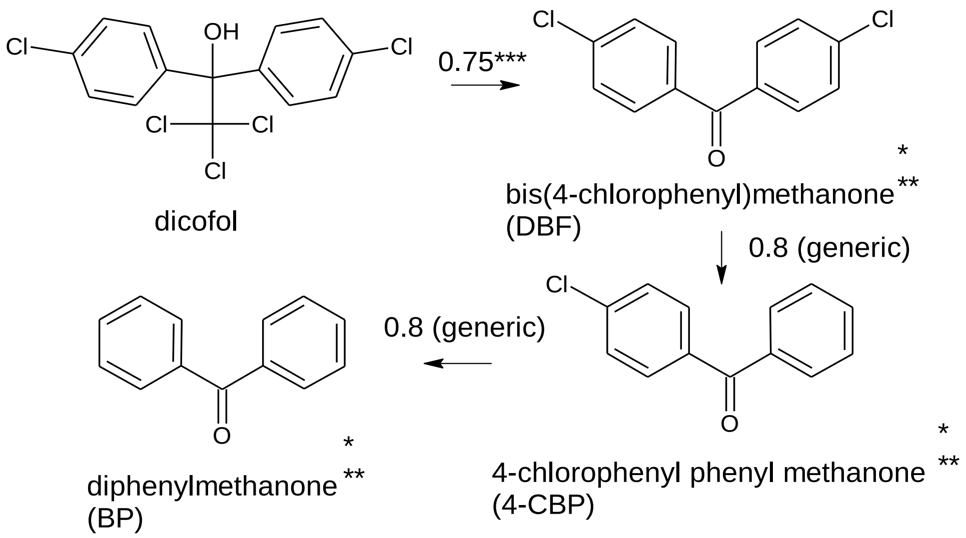


Figure 4.13. Degradation scheme of dicofol (Debabrata & Sivakumar, 2018*; Oliveira et al., 2012***; Yu et al., 2008**). Number on each arrow indicates the fraction of formation of TP.

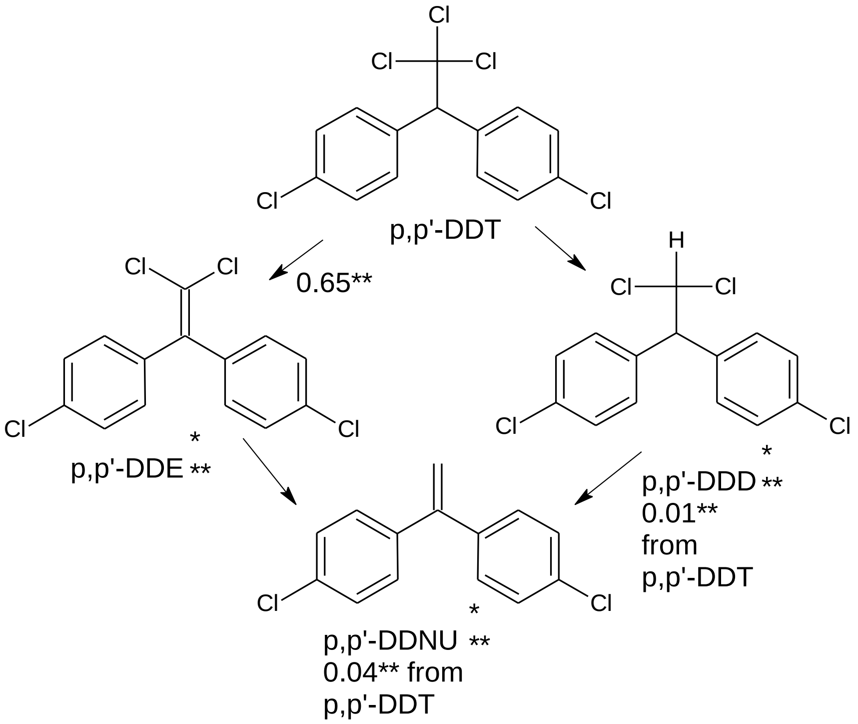


Figure 4.14. Degradation scheme of p, p'-DDT (Huang et al., 2018*; Lin & Chang, 2007**) with the fraction of formation.

4.3.2 Physicochemical Properties for Dicofol and DDT Families

Compiled literature derived physicochemical property and EPI Suite predicted inputs of parent chemicals and TPs are presented in Appendix A-Table A1. FAVs for parent chemicals and their TPs are given in Appendix A- Table A2.

4.3.3 Evaluation and Persistency of Dicofol Family

Table 4.9. shows the environmental mass distribution of the substance family, total mass, and persistence. All members of the family overwhelmingly end up in the soil media when introduced into air, soil, or all three media equally. However, if mode-of-entry is water, then steady-state compound mass seems to reside in the water phase, almost exclusively. A considerable amount of the TPs also ends up in the air

phase when introduced into air, with 5%, 14%, and 37% of the TP residing in air. The vapor pressure of each TP is an order of magnitude greater than the one before, with increasing VPs from DBF to 4-CBP to BP. Soil and water run-off from soil to water is an important intermedia transport mechanism for all members of this family. Also, net transfer from soil to air medium via diffusion is a considerable mechanism for DBF, 4-CBP, and BP.

Based on Table 4.9, the environmental mass of compounds was plotted in various media under several emission scenarios in Figure 4.15. The higher persistence of DBF is evident from the figure, where a much higher mass of DBF resides in the environment, especially in soil, when compared to dicofol or the others. Any member from dicofol family emission to only water or only soil medium could be a reason for observing the highest amount of the compound in the emitted medium.

Table 4.9. Amount of dicofol & its TPs as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
Dicofol	Air	0.00E+00	0	8.69E+04	12	6.10E+05	88	1.73E+02	0	6.97E+05	697
	Water	0.00E+00	0	1.43E+05	100	0.00E+00	0	2.84E+02	0	1.43E+05	143
	Soil	0.00E+00	0	8.07E+04	11	6.78E+05	89	1.60E+02	0	7.59E+05	759
	All three	0.00E+00	0	1.03E+05	19	4.29E+05	81	2.06E+02	0	5.33E+05	533
DBF	Air	6.54E+04	5	1.37E+05	11	1.01E+06	83	1.17E+04	1	1.23E+06	1636
	Water	9.10E+02	0	1.52E+06	91	1.41E+04	1	1.30E+05	8	1.67E+06	2226
	Soil	4.87E+02	0	5.56E+04	2	2.99E+06	98	4.75E+03	0	3.05E+06	4069
	All three	2.23E+04	1	5.72E+05	29	1.34E+06	68	4.89E+04	2	1.98E+06	2644
4-CBP	Air	5.55E+04	14	5.40E+04	14	2.73E+05	71	2.33E+03	1	3.84E+05	641
	Water	9.00E+02	0	7.64E+05	95	4.42E+03	1	3.30E+04	4	8.02E+05	1337
	Soil	4.46E+02	0	2.75E+04	2	1.49E+06	98	1.19E+03	0	1.52E+06	2538
	All three	1.89E+04	2	2.82E+05	31	5.90E+05	65	1.22E+04	1	9.03E+05	1505
BP	Air	4.14E+04	37	1.41E+04	12	5.75E+04	51	2.66E+02	0	1.13E+05	236
	Water	3.86E+02	0	2.47E+05	98	5.37E+02	0	4.65E+03	2	2.52E+05	525
	Soil	2.18E+02	0	5.71E+03	1	4.85E+05	99	1.08E+02	0	4.91E+05	1023
	All three	1.40E+04	5	8.88E+04	31	1.81E+05	63	1.67E+03	1	2.86E+05	595

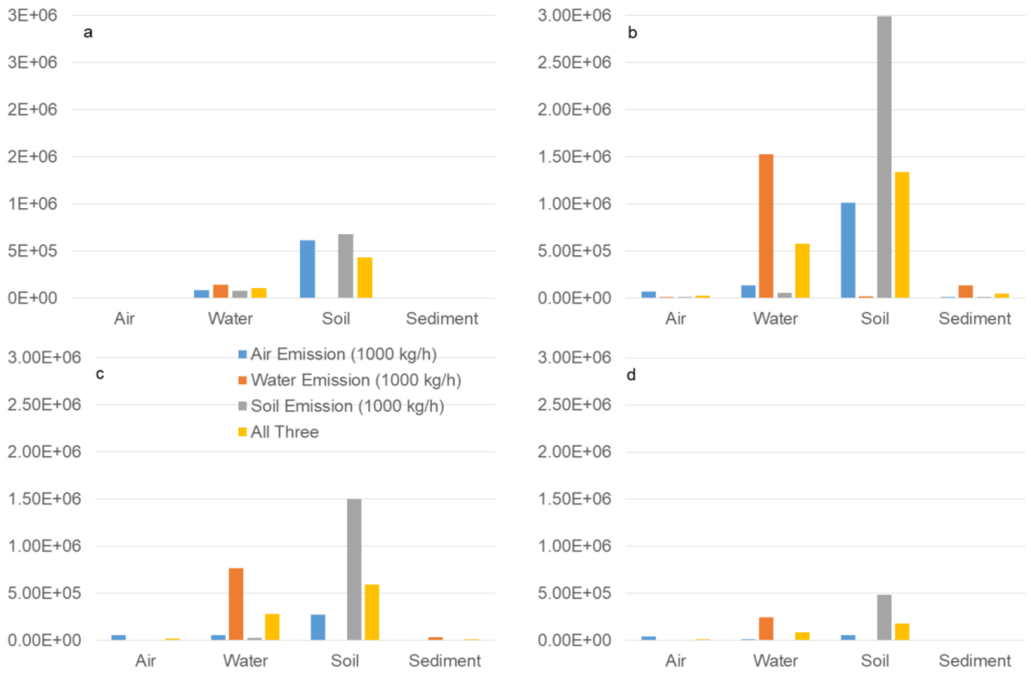


Figure 4.15. Amount (kg) of (a) dicofol, (b) DBF, (c) 4-CBP, and (d) BP in the environment.

Individual persistence of dicofol which is likely to be detected in soil since it is a pesticide and secondary persistence of its TPs when soil is the mode-of-entry, along with their JP, are represented in Figure 4.16. DBF is the TP with the highest persistence among all compounds of the dicofol family, as can be understood from the last column of Table 4.9. Considering this fact, as well as that DBF has the highest emission amount within TPs– being the first TP from dicofol, it has the highest secondary persistence among all TPs. By looking at the figure, it can be seen that the persistence of dicofol is increased considerably when degradation products are considered. Two of the TPs, DBF, and 4-CBP have higher persistence than dicofol. DBF is more than three times persistent than dicofol. Also, 4-CBP is more than two times persistent than dicofol. These findings show that even though dicofol does not pose a risk due to its persistence, its TPs, especially DBF and 4-CBP fall under the persistent category according to Webster et al. (1998) criterion.

Nevertheless, as will be seen in the results for DDT and its TPs in the next section, the dicofol family is indeed much less persistent when compared to the DDT family.

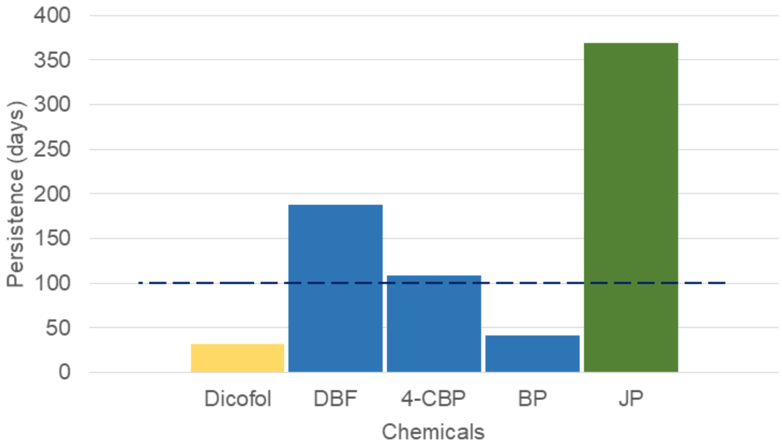


Figure 4.16. Persistence of dicofol family with a dashed line that is P_{ov} criterion of 100 days (Webster et al., 1998).

The predictive capability of EPI Suite and the effects of physicochemical inputs on chemical amount and persistence can be observed in Table 4.10. Even though up to five orders of magnitude difference are present between FAV and EPI Suite predicted physicochemical parameters, none results in a change in the persistence of dicofol. On the other hand, percent differences between EPI Suite predicted and FAV for half-life in air, water, and the soil are indicated by seven, four, and three orders of magnitude, respectively. Only half-life in water and soil causes a change in chemical amount and persistence. Overall, half-life in water and soil should be detected carefully to correctly estimate dicofol persistence.

Table 4.10. FAV and EPI Suite predicted inputs on atrazine amount and persistence with percentage difference.

Chem	FAV	EPI Suite Value	Diff. Btw Inputs as %	Chem Amount (mole)	Persistence (d)	Percent Diff (%)
dicofol				2.05E+06	32	
dicofolmeltpred	7.80E+01	1.48E+02	-90	2.05E+06	32	0
dicofolvaporpred	7.03E-06	1.58E-06	78	2.05E+06	32	0
dicofolsolubpred	6.07E+00	1.78E+00	71	2.05E+06	32	0
dicofolHenrypred	4.29E-04	3.29E-04	23	2.05E+06	32	0
dicofolairhalfpred	8.11E-04	7.50E+01	-9247742	2.05E+06	32	0
dicofolwaterpred	9.90E+01	4.32E+03	-4264	1.14E+07	175	82
dicofolsoilpred	1.08E+03	8.64E+03	-700	3.31E+06	51	38
dicofollogKowpred	3.20E+00	4.85E+00	-52	2.05E+06	32	0
dicofolKocpred	5.01E+03	1.27E+04	-153	2.05E+06	32	0
dicofolpredicted				1.83E+07	283	89

The sensitivity analysis for the dicofol family, when soil is the mode-of-entry, is represented in Figure 4.17. According to this figure, half-life in soil and water are sensitive parameters for dicofol as was deduced from the results presented in the aforementioned Table 4.10. While half-life in soil gains considerable importance, half-life in water loses importance for all TPs. Although the solubility of TPs increases by an order of magnitude from DBF to 4-CBP to BP, when mode-of-entry is soil, more than 98% of each compound resides in soil (Table 4.9). Subsequently, persistence of TPs is more sensitive to half-life in soil when compared to half-life in water.

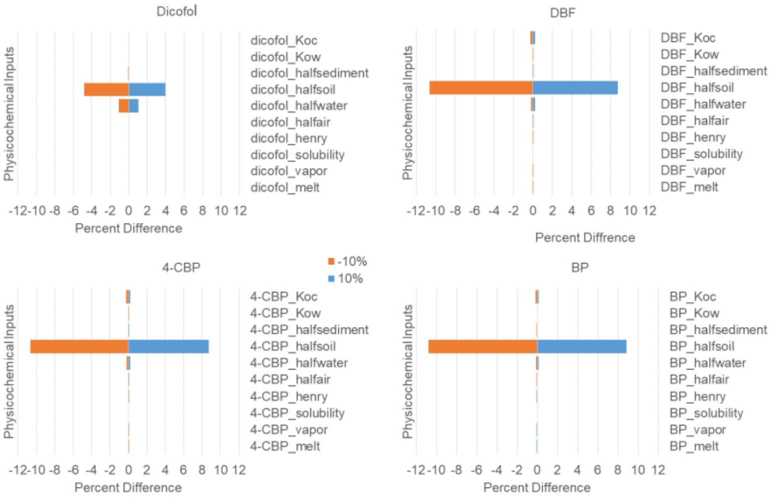


Figure 4.17. Percent difference impact on persistence upon 10% change in physicochemical parameter values for dicofol, DBF, 4-CBP, and BP.

4.3.4 Evaluation and Persistence of DDT Family

Table 4.11 demonstrates the environmental mass distribution of the substance family, total mass, and persistence. As is apparent from this table, p, p'-DDT mainly accumulates in soil and sediment from soil to water run-off and net transfer from water to sediment. Similar to DDT, all TPs are likely to accumulate in soil and sediment media. However, DDNU percentage in the air is higher compared to other members of the DDT family, owing to its orders of magnitude higher (e.g. three orders of magnitude greater than DDT) vapor pressure. DDNU distribution into water media could support more hydrophilic characteristics compared to others as indicated by its lower K_{ow} and higher solubility (as can be seen in Appendix A Table-A2).

Based on Table 4.11, the environmental mass of compounds was plotted regarding several media under different emission scenarios in Figure 4.18. According to Figure 4.18, p, p'- DDT, p, p'- DDE, and p, p'- DDD emissions into the soil are the main reasons for high concentrations of these chemicals in the soil medium. P, p'-DDT is the most persistent compound of the family, as can be deduced from the last column of Table 4.11. DDNU is the most affected compound from the mode-of-entry. This is because the percent mass distribution in each media differs very much from one mode of entry, e.g. air, to another, e.g. soil. The very low atmospheric half-life of DDNU (i.e. 1 hr) results in a very low persistence (i.e. 4 hours as shown in the last column of Table 4.11) when the compound is introduced into air, i.e. mode-of-entry is air.

Table 4.11. Amount of p, p’- DDT & its TPs as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
DDT	Air	9.80E+02	0	2.37E+03	1	3.07E+05	76	9.38E+04	23	4.04E+05	22467
	Water	1.19E+02	0	2.56E+04	2	3.73E+04	3	1.01E+06	94	1.08E+06	59807
	Soil	8.16E-01	0	8.94E+01	0	4.40E+05	99	3.54E+03	1	4.44E+05	24652
	All three	3.67E+02	0	9.35E+03	1	2.62E+05	41	3.70E+05	58	6.42E+05	35642
DDE	Air	5.33E+02	2	3.94E+02	2	1.66E+04	69	6.43E+03	27	2.39E+04	2044
	Water	2.64E+02	0	1.67E+04	6	8.18E+03	3	2.73E+05	92	2.98E+05	25488
	Soil	3.21E+00	0	1.02E+02	0	3.45E+05	99	1.66E+03	0	3.46E+05	29605
	All three	2.67E+02	0	5.74E+03	3	1.23E+05	55	9.37E+04	42	2.23E+05	19046
DDD	Air	8.33E+00	1	1.71E+01	1	9.78E+02	76	2.83E+02	22	1.29E+03	9661
	Water	1.20E+00	0	3.21E+02	6	1.41E+02	2	5.32E+03	92	5.78E+03	43380
	Soil	1.63E-02	0	2.08E+00	0	4.20E+03	99	3.45E+01	1	4.23E+03	31775
	All three	3.18E+00	0	1.13E+02	3	1.77E+03	47	1.88E+03	50	3.77E+03	28272
DDNU	Air	8.53E-01	30	2.46E-01	9	3.72E-01	13	1.33E+00	48	2.80E+00	4
	Water	3.61E-01	0	4.99E+02	16	1.57E-01	0	2.70E+03	84	3.20E+03	4808
	Soil	1.36E-03	0	5.74E-01	0	2.76E+03	100	3.11E+00	0	2.77E+03	4152
	All three	4.05E-01	0	1.67E+02	8	9.21E+02	46	9.02E+02	45	1.99E+03	2988

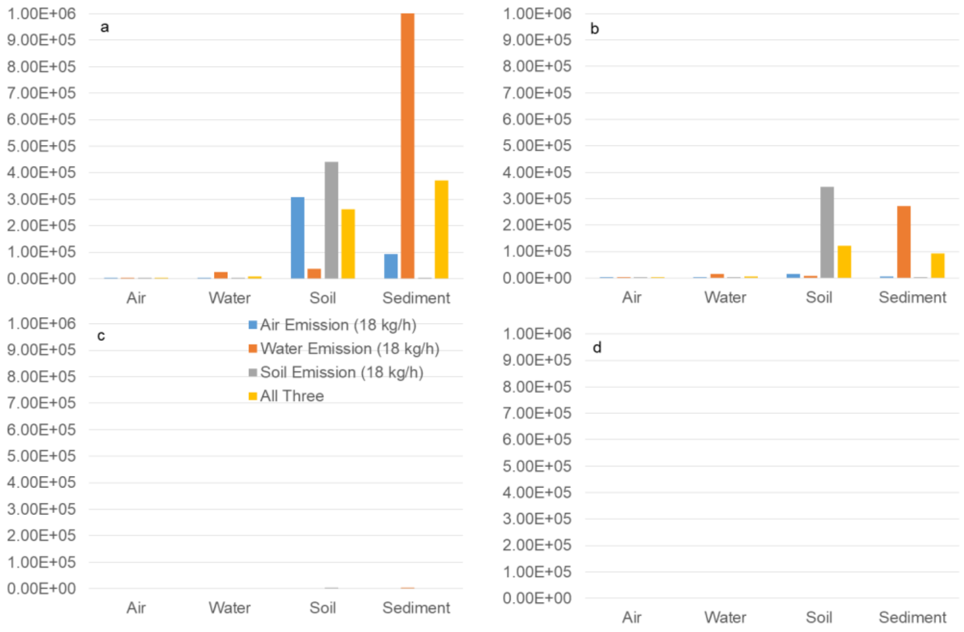


Figure 4.18. Amount (kg) of (a) p, p’- DDT, (b) p, p’- DDE, (c) p, p’- DDD, and (d) p, p’- DDNU in the environment.

Individual persistence of p, p’-DDT and its TPs, together with their joint persistence are demonstrated in Figure 4.19. As can be seen from this figure, DDT has much higher persistence when compared to its TPs and it is the main contributor to joint persistence. P, p’-DDT exceeds the overall persistence threshold value on its own, so joint persistence is also much higher than 100 days. P, p’-DDD and p, p’- DDE are less persistent compared to p, p’-DDT, so their contribution to joint persistence is not as important as the contribution of DDT. A similar finding was also reported by Schenker et al. (2007).

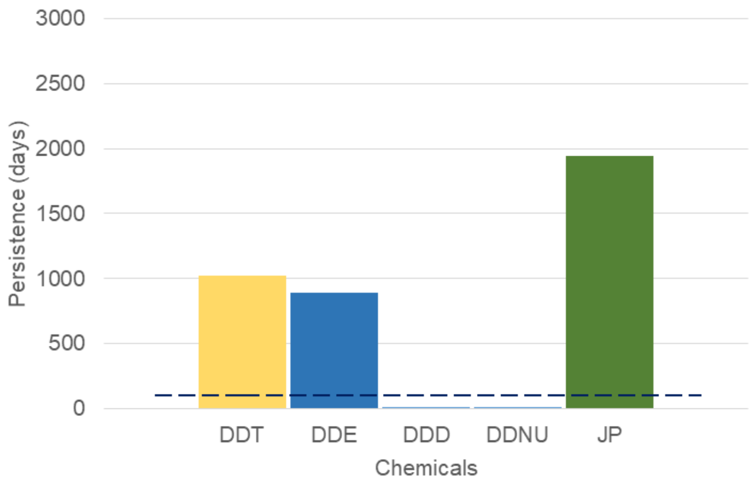


Figure 4.19. Persistence of p, p’-DDT family with a dashed line that is P_{ov} criterion of 100 days (Webster et al., 1998).

EPI Suite predicted versus FAVs with total p, p’-DDT amount and persistence values are shown in Table 4.12. The percentage differences between EPI Suite predicted and FAV for melting point, vapor pressure, solubility, partition coefficients, and half-lives except half-life in soil do not generate any change on environmental mass and persistence even if the difference is up to five orders of magnitude. On the other hand, two orders of magnitude percentage difference in soil half-life cause two orders of magnitude difference in persistence and environmental mass. Since mode-of-entry here is soil, and p, p’- DDT resides in soil more than 98%, making soil half-life the most influential parameter affecting its persistence. In brief, half-life in soil should be determined carefully as much as possible for the persistence evaluation of p, p'-DDT.

Table 4.12. FAV and EPI Suite predicted inputs on p,p'-DDT amount and persistence with percentage difference.

Chem	**FAV**	**EPI Suite Value**	**Diff. Btw Inputs as %**	**Chem Amount (mole)**	**Persistence (d)**	**Percent Diff (%)**
DDT				1.25E+06	1027	
DDTmeltpred	1.09E+02	1.23E+02	-13	1.25E+06	1027	0
DDTvaporpred	2.01E-05	1.16E-02	-57611	1.25E+06	1027	0
DDTsolubpred	5.47E-03	9.51E-02	-1639	1.25E+06	1027	0
DDTHenrypred	1.30E+00	4.31E+01	-3215	1.25E+06	1022	0
DDTairhalfpred	1.70E+02	7.50E+01	56	1.25E+06	1027	0
DDTwaterpred	5.50E+03	4.32E+03	21	1.25E+06	1027	0
DDTsoilpred	1.70E+04	8.64E+03	49	6.37E+05	523	-96
DDTsedpred	5.50E+04	3.89E+04	29	1.25E+06	1025	0
DDTlogKowpred	6.13E+00	6.69E+00	-9	1.25E+06	1027	0
DDTKocpred	2.51E+05	1.69E+05	33	1.25E+06	1027	0
DDTpredicted				6.30E+05	517	-99

Sensitivity analysis for this family is presented in Figure 4.20 with soil as the mode-of-entry for the compounds. By looking at this figure, it can be said that half-life in soil is the most sensitive parameter for all members, excluding the vapor pressure decrease of DDT.

This is consistent with the findings of Table 4.12. A similar interesting outcome as that of HA is also observed for p, p'-DDT when its vapor pressure is changed. A 10% increase/decrease in vapor pressure of p, p'-DDT surprisingly changes its persistence to the same extent; about 180% reduction in persistence. There are a few other compounds in the coming sub-chapters where similar results are observed. Some discussion is attempted regarding in the final overall evaluation section.

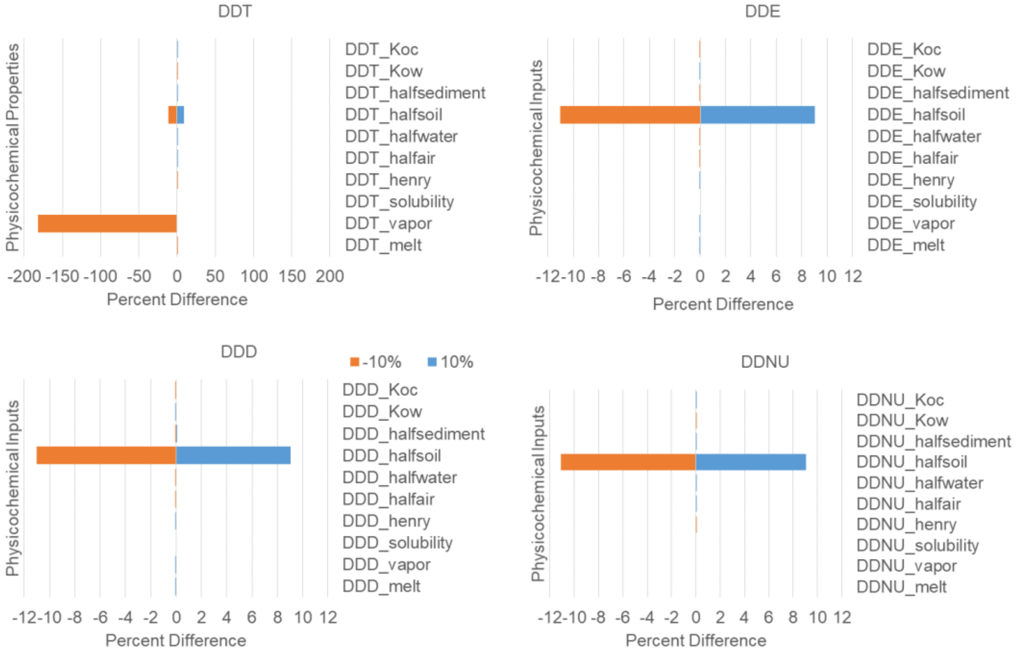


Figure 4.20. Sensitivity analysis result for p, p’-DDT and its TPs, namely, DDE, 4-DDD, and DDNU.

4.4 DEHP

Because of the fluidity and stability of phthalate ester, it is used in an additive form to impart flexibility in resins such as polyvinylchloride, polyurethanes, and polyvinyl acetates. Plasticizers are utilized in furnishing, building materials, medical equipment, and packaging (Staples et al., 1997). DEHP is a member of the phthalate ester group and is widely used as an industrial chemical (Vicent et al., 2013). It is unbound to polymers, so it can mobilize (Cheng et al., 2008). The accumulation tendency of DEHP in sewage sludge can pose some risks for the environment and public in the case of sludge land application (Vicent et al., 2013). According to the U.S. EPA, it is classified as a B2 class which means a probable human carcinogen. Also, it has endocrine disruptor characteristic (Vicent et al., 2013). Hence, the investigation fate of DEHP and its TPs could be promising.

4.4.1 Degradation Pathway Scheme for DEHP

DEHP was shown to be fully degraded by *Gordonia* sp. Lff in contaminated soil (Wang et al., 2019). In biochemical degradation pathways of DEHP, mono-ethylhexyl phthalate (MEHP) is one of the major intermediate compounds. In addition to MEHP, phthalic acid (PA) is a common transformation product from DEHP degradation media where microorganisms are present. DEHP degradation by the strain may be explained via β-oxidation and ester hydrolysis (Wang et al., 2019). Figure 4.21 demonstrates the degradation scheme of DEHP.

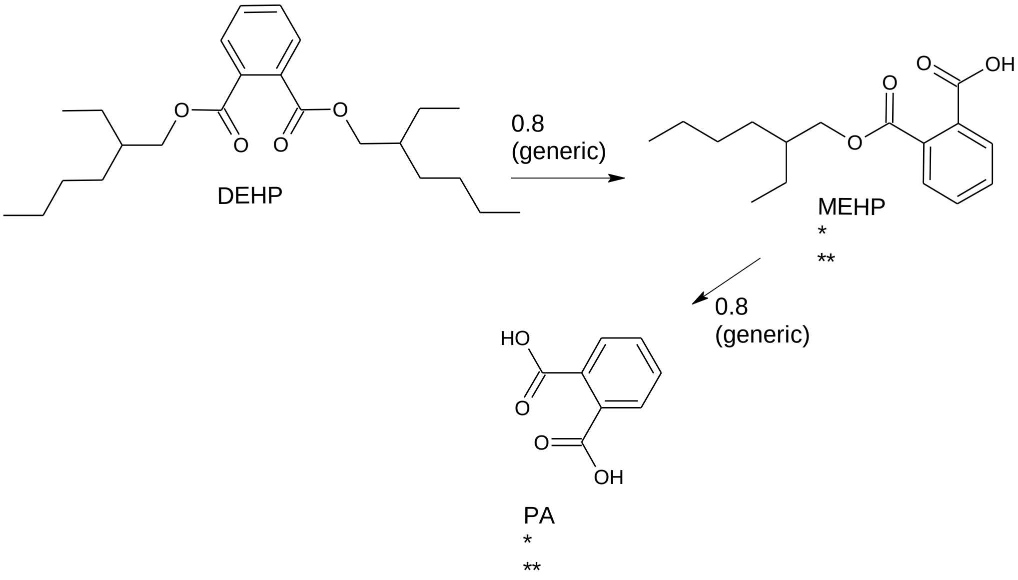


Figure 4.21. Degradation scheme of DEHP (Magdouli et al., 2013*; Wang et al., 2019**). Number on each arrow indicates the fraction of formation of TP.

4.4.2 Physicochemical Properties for DEHP Family

Compiled literature derived physicochemical property of parent chemical and EPI Suite predicted TPs are presented in Appendix A-Table A1. FAVs for parent chemical and its TPs are given in Appendix A-Table A2.

4.4.3 Evaluation and Persistency of DEHP Family

Table 4.13 indicates the environmental mass distribution of the substance family, total mass, and persistence. For all modes of entry except water, soil is the dominant medium for DEHP, MEHP, and PA. This can be explained by their significantly high log K_{ow} and K_{oc} values. When introduced into water, sediment deposition is a significant intermedia transport mechanism for DEHP deposition. While diffusion between soil and air is important for DEHP and MEHP, soil and water run-off from soil to water medium is considerable for PA. For MEHP and PA, when introduced into water, they tend to remain in water. PA has the smallest VP and the highest solubility among all family members, which results in no partitioning into air and a very limited intermedia transport from the water media. This results in 100% of PA accumulating in water.

Table 4.13 Amount of DEHP & its TPs as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
DEHP	Air	6.87E+04	41	4.88E+03	3	8.84E+04	52	7.22E+03	4	1.69E+05	169
	Water	1.28E+04	3	1.75E+05	38	1.65E+04	4	2.59E+05	56	4.63E+05	463
	Soil	2.68E+01	0	3.01E+01	0	7.93E+05	100	4.45E+01	0	7.93E+05	793
	All three	2.72E+04	6	5.99E+04	13	2.99E+05	63	8.86E+04	19	4.75E+05	475
MEHP	Air	1.26E+04	19	4.54E+03	7	4.94E+04	74	1.73E+02	0	6.67E+04	83
	Water	4.58E+02	0	3.99E+05	96	1.80E+03	0	1.52E+04	4	4.16E+05	520
	Soil	2.20E+01	0	4.09E+02	0	8.29E+05	100	1.56E+01	0	8.29E+05	1037
	All three	4.35E+03	1	1.35E+05	31	2.93E+05	67	5.14E+03	1	4.38E+05	547
PA	Air	0.00E+00	0	1.72E+05	35	3.21E+05	65	3.17E+02	0	4.93E+05	771
	Water	0.00E+00	0	3.32E+05	100	0.00E+00	0	6.12E+02	0	3.33E+05	520
	Soil	0.00E+00	0	1.54E+05	30	3.56E+05	70	2.84E+02	0	5.11E+05	798
	All three	0.00E+00	0	2.20E+05	49	2.26E+05	51	4.05E+02	0	4.46E+05	696

By considering Table 4.13, the environmental mass distribution of DEHP, MEHP, and PA was plotted regarding several media in case of diverse emission scenarios in Figure 4.22. The mode-of-entry effect can be observed for DEHP emission into the soil. It means that DEHP emission into soil causes a much higher amount of DEHP in soil medium (i.e. approximately 8E+05 kg) when compared to other media.

Similar to this case, MEHP emission into only water and only soil medium cause high MEHP mass in water and soil medium, respectively. Furthermore, mode-of-entry can be detected in PA emission into only water and only soil medium. Mass distribution due to air emission is not affected by mode-of-entry regardless of members of this family.

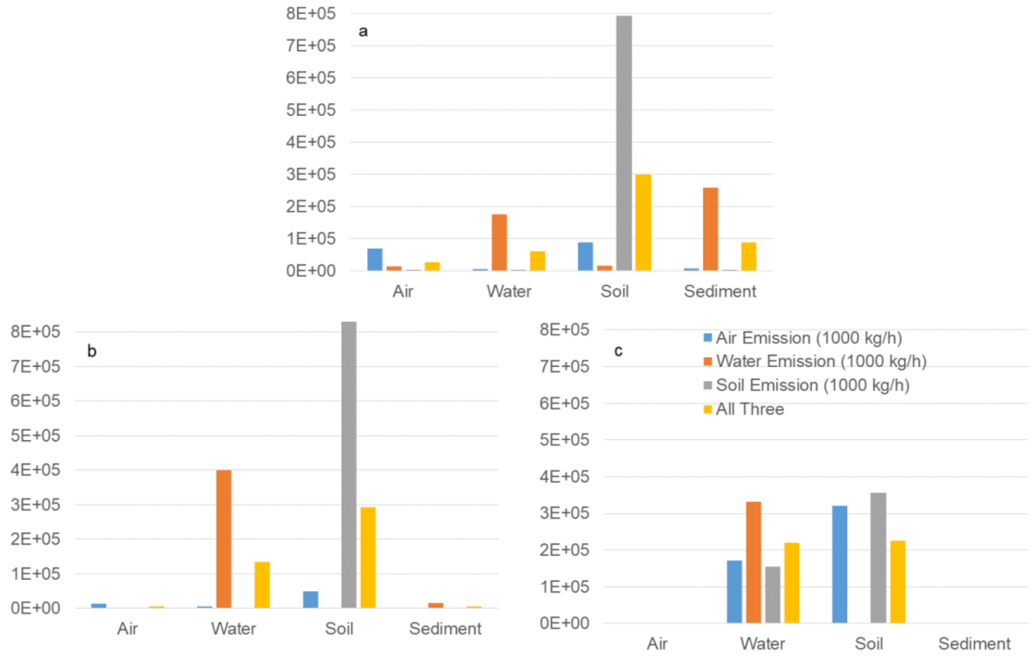


Figure 4.22. Amount (kg) of (a) DEHP, (b) MEHP, and (c) PA in the environment.

The primary persistence of DEHP, secondary persistence of MEHP, and PA are demonstrated in Figure 4.23 along with the joint persistence of this substance family. The persistence of DEHP is increased remarkably when degradation products are included. The contribution of MEHP and PA to joint persistence is higher than DEHP. This is mainly dictated by the high degradation half-lives (as predicted by EPI Suite) of TPs in soil (i.e. 720 days) compared to the half-life of DEHP in soil (i.e. 550 days). To be brief, joint persistence is more than two times higher than primary persistence. This new metric (joint persistence) exceeds threshold value while primary persistence is very much lower than the threshold value. Results indicate that both TPs of DEHP should be monitored in the natural environment.

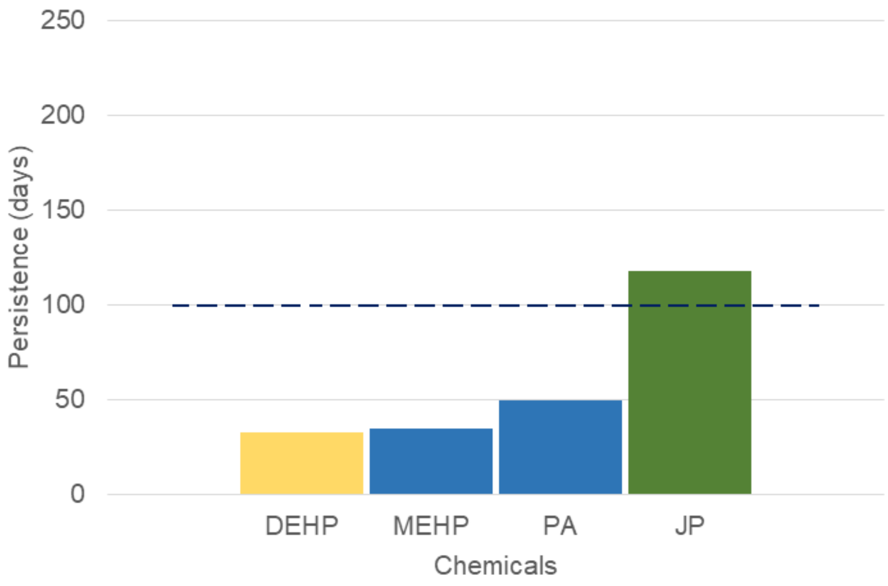


Figure 4.23. Persistence of DEHP family with a dashed line that is P_{ov} criterion of 100 days (Webster et al., 1998).

The predictive capability of EPI Suite and the effects of physicochemical inputs on chemical amount and persistence can be understood from Table 4.14. While the percentage difference between EPI Suite predicted and FAVs for many parameters do not generate any difference in persistence and chemical amount, half-life in soil has the greatest impact on persistence. This is consistent with the aforementioned outcomes showing to DEHP mainly accumulating in soil.

Table 4.14. Effect of FAV and EPI Suite predicted inputs on DEHP amount and persistence with percentage difference.

Chem	FAV	EPI Suite Value	Diff. Btw Inputs as %	Chem Amount (mole)	Persistence (d)	Percent Diff (%)
DEHP				2.03E+06	33	
DEHPmeltpred	-5.00E+01	6.40E+01	228	2.03E+06	33	0
DEHPvaporpred	1.91E-03	3.06E-04	84	2.03E+06	33	0
DEHPsolubpred	2.89E-02	1.13E-02	61	2.03E+06	33	0
DEHPHenrypred	2.59E+01	1.06E+01	59	2.03E+06	33	0
DEHPairhalfpred	5.50E+01	1.20E+01	78	2.03E+06	33	0
DEHPwaterpred	1.70E+02	3.60E+02	-112	2.03E+06	33	0
DEHPsoilpred	5.50E+02	7.20E+02	-31	2.66E+06	43	24
DEHPsedpred	1.70E+03	3.24E+03	-91	2.03E+06	33	0
DEHPlogKowpre	5.91E+00	8.27E+00	-40	2.03E+06	33	0
DEHPKocpred	1.00E+05	1.20E+05	-20	2.03E+06	33	0
DEHPpredicted				2.66E+06	43	24

The sensitivity analysis for the DEHP family is shown in Figure 4.24. It is apparent from this figure that half-life in soil is the sensitive parameter for all members of this family. Half-life in soil has similar sensitivity in DEHP and MEHP persistence calculation. On the other hand, half-life in soil is less sensitive in PA persistence. It is noteworthy that while all members of the DEHP family is sensitive to changes in soil half-life, PA is additionally sensitive to half-life in water. This is because aqueous solubility of PA is six orders of magnitude greater than DEHP and MEHP. Also, while a ten percent decrease in vapor pressure causes a noticeable change, a ten percent increase does not have any effect on persistence.

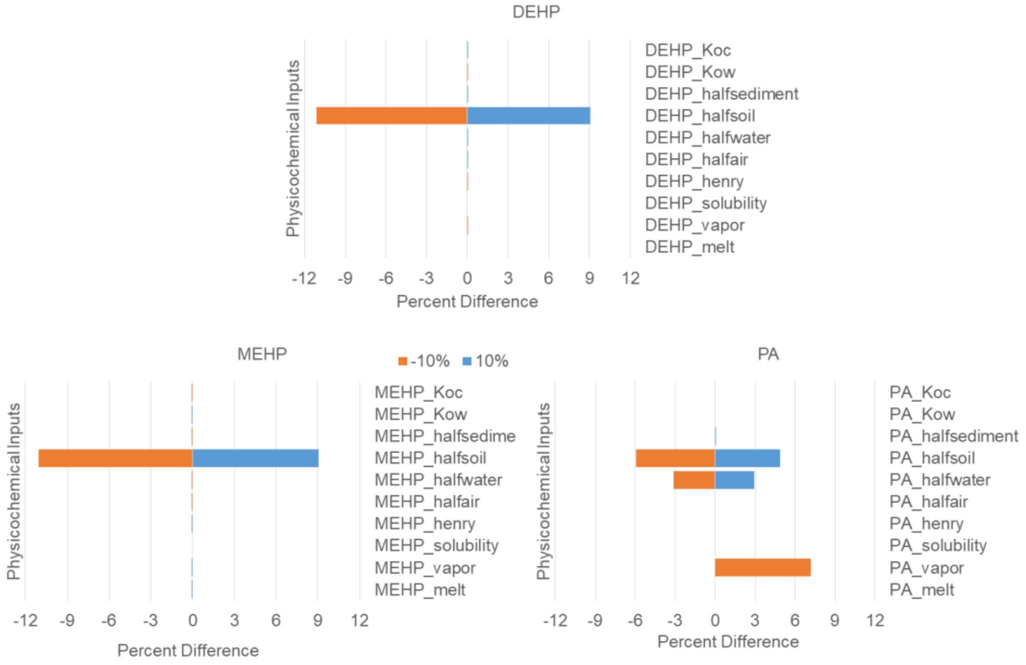


Figure 4.24. Sensitivity analysis result for DEHP and its TPs, namely, MEHP and PA.

4.5 BDE-153

PBDEs are a brominated chemical group that is deliberately produced as flame retardants. This group is widely used in textile, plastic, upholstery, electrical and electronic industries. PBDEs is an attention-grabbing group for policymakers and scientist due to increasing levels in them since the 1970s along with their long-term environmental problem (Fang et al., 2008). PBDEs might have negative effects on human health due to their structural similarity to PCBs. According to the number and location of the bromine atom(s), there are 209 possible congeners (USEPA, 2010). However, BDE-28, 47, 99, 100, 153, and 154 were labeled as priority pollutants in EU WFD 2008/105/EC and Appendix 5 of the Surface Water Quality Management Regulation (in Turkish).

In this study, BDE-153 was selected from this subgroup of six PBDEs. Since BDE-153 contains six bromine atoms, so other priority congeners except BDE-154 could be formed from BDE-153. According to Pan et al. (2016), BDE-153, and 154 forms in the same step and they have many common TPs. By considering data availability in the literature, BDE-153 was preferred rather than BDE-154. Understanding likely debromination pathways for BDE-153 would be significant to evaluate its integrated persistence.

4.5.1 Degradation Pathway Scheme for BDE-153

Photodegradation of BDE-153 under UV light causes consecutive reductive debromination in hexane. BDE-153 photolysis begins with a loss of one bromine atom to generate three pentaBDEs namely BDE-101, BDE-99, and BDE-118. Congeners with a lower number of bromine atoms occur in succession when irradiation continues. Photoproducts were detected as debromination from ortho-, meta-, or para-substituted positions. To consider the effects of photodegradation, the bromine substitution pattern becomes more important for congeners with a high number of bromine atoms. In the second generation, BDE-52, 49, 47, 66, and 77 form. Bromine loss from BDE-99 of ortho, meta, and para position leads to the formation of BDE-49, 47, and 66, respectively (Fang et al., 2008). Additionally, BDE-118, 99, 101, 66, 47, and 49 are stated as main photoproducts of BDE-153 (Wei et al., 2013). Figure 4.25 shows the degradation scheme for BDE-153, with the fraction of formation information provided for each TP on the arrows.

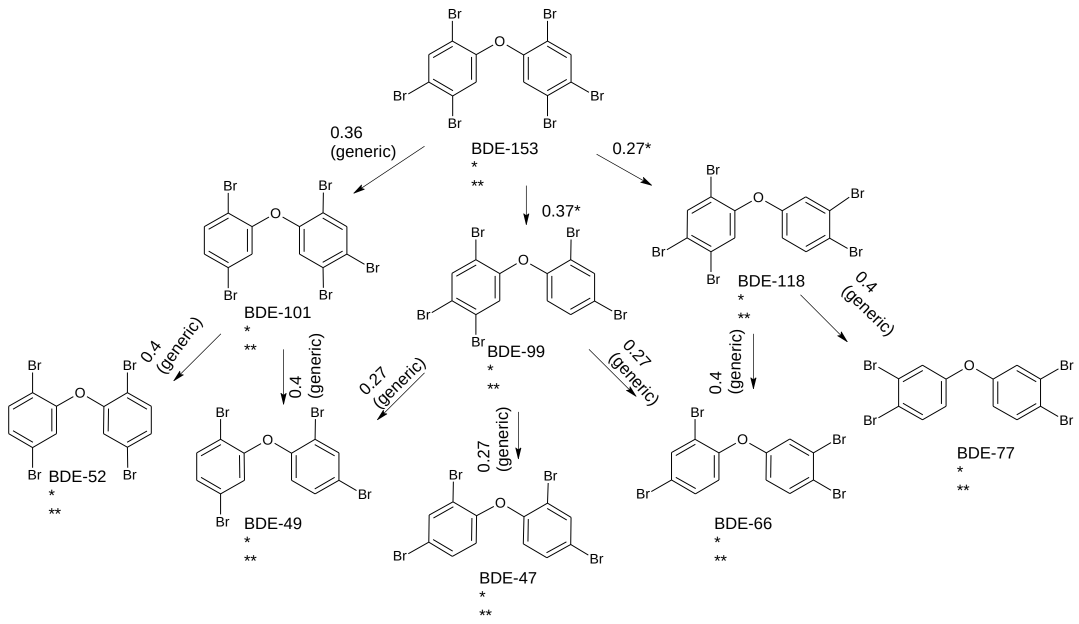


Figure 4.25. Degradation scheme of BDE-153 (Fang et al., 2008*; Pan et al., 2016**). Number on each arrow indicates fraction of formation of TP.

4.5.2 Physicochemical Properties for BDE-153 Family

Compiled literature derived and EPI Suite estimated physicochemical properties of parent chemical and TPs are presented in Appendix A- Table A1. FAVs for parent chemical and its TPs are given in Appendix A- Table A2.

4.5.3 Evaluation and Persistency of BDE-153 Family

Table 4.15 demonstrates the environmental mass distribution of the BDE-153 family, total mass, and persistence. BDE-153 distributes into primarily soil and sediment depending on the emission scenario. Dominant medium changes with respect to half-life in sediment medium. If half-life in sediment that was stated in Zhu et al. (2014) was taken, soil could have been the dominant medium. This is because Zhu et al. (2014) report half-life in sediment for BDE-153 and BDE-47 as 1120, and 1549, respectively. These two half-lives are much smaller than the ones used in sediment for this study, i.e. 38900 hours. Similar to BDE-153, soil, or sediment for TPs is the dominant medium with less amounts in the air.

When TPs of BDE-153, i.e. lower brominated BDEs are reviewed, it can be seen that while some accumulate more in water (e.g. BDE-101, 118, 52) others prefer soil or sediment much more (e.g. BDE-99, 47, 66). This can be traced back to their K_{oc} values, where the former group has an order of magnitude lower K_{oc} values, resulting in their higher aqueous phase distribution. Another possible explanation could be that the former group is infrequently studied while latter ones are much more studied in the literature.

Table 4.15. Amount of BDE-153 & its TPs as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
BDE-153	Air	7.98E+04	0	6.78E+04	0	1.04E+07	63	6.02E+06	36	1.65E+07	16538
	Water	1.41E+02	0	5.73E+05	1	1.84E+04	0	5.09E+07	99	5.15E+07	51477
	Soil	8.83E-01	0	7.36E+02	0	1.25E+07	99	6.53E+04	1	1.25E+07	12518
	All three	2.67E+04	0	2.14E+05	1	7.61E+06	28	1.90E+07	71	2.68E+07	26844
BDE-118	Air	6.69E+04	3	1.90E+05	8	1.66E+06	68	5.33E+05	22	2.45E+06	9176
	Water	9.31E+03	0	1.12E+06	25	2.32E+05	5	3.14E+06	70	4.51E+06	16850
	Soil	1.75E+02	0	8.33E+03	0	3.31E+06	99	2.34E+04	1	3.34E+06	12494
	All three	2.55E+04	1	4.40E+05	13	1.73E+06	51	1.23E+06	36	3.43E+06	12840
BDE-101	Air	1.00E+05	3	2.74E+05	9	2.09E+06	67	6.41E+05	21	3.10E+06	8541
	Water	1.58E+04	0	1.56E+06	28	3.31E+05	6	3.65E+06	66	5.55E+06	15267
	Soil	2.92E+02	0	1.16E+04	0	4.50E+06	99	2.73E+04	1	4.54E+06	12481
	All three	3.87E+04	1	6.14E+05	14	2.31E+06	52	1.44E+06	33	4.40E+06	12096
BDE-99	Air	3.78E+04	1	2.42E+04	0	3.36E+06	60	2.23E+06	39	5.65E+06	15302
	Water	2.75E+02	0	2.04E+05	1	2.45E+04	0	1.88E+07	99	1.90E+07	51424
	Soil	9.64E-01	0	2.64E+02	0	4.60E+06	99	2.43E+04	1	4.62E+06	12518
	All three	1.27E+04	0	7.60E+04	1	2.66E+06	27	7.00E+06	72	9.75E+06	26415
BDE-77	Air	1.73E+04	2	5.37E+04	7	6.07E+05	77	1.15E+05	15	7.93E+05	7416
	Water	3.74E+03	0	4.34E+05	29	1.31E+05	9	9.29E+05	62	1.50E+06	14003
	Soil	8.99E+01	0	4.89E+03	0	1.32E+06	99	1.05E+04	1	1.33E+06	12470
	All three	7.05E+03	1	1.64E+05	14	6.86E+05	57	3.52E+05	29	1.21E+06	11296
BDE-66	Air	4.77E+04	2	1.90E+04	1	5.91E+05	30	1.35E+06	67	2.00E+06	9798
	Water	1.03E+03	0	1.41E+05	1	1.28E+04	0	9.99E+06	98	1.01E+07	49613
	Soil	3.72E+00	0	1.98E+02	0	2.55E+06	99	1.40E+04	1	2.56E+06	12519
	All three	1.62E+04	0	5.35E+04	1	1.05E+06	21	3.78E+06	77	4.90E+06	23977
BDE-52	Air	4.19E+04	9	6.39E+04	14	2.21E+05	50	1.17E+05	26	4.44E+05	3053
	Water	1.77E+04	1	4.62E+05	32	9.32E+04	7	8.48E+05	60	1.42E+06	9776
	Soil	3.95E+02	0	5.34E+03	0	1.79E+06	99	9.81E+03	1	1.80E+06	12393
	All three	2.00E+04	2	1.77E+05	14	7.00E+05	57	3.25E+05	27	1.22E+06	8407
BDE-49	Air	6.88E+04	9	1.12E+05	14	4.17E+05	52	2.05E+05	25	8.03E+05	3305
	Water	2.71E+04	1	8.07E+05	33	1.64E+05	7	1.47E+06	60	2.47E+06	10166
	Soil	6.06E+02	0	9.30E+03	0	2.98E+06	99	1.70E+04	1	3.01E+06	12401
	All three	3.22E+04	2	3.09E+05	15	1.19E+06	57	5.64E+05	27	2.09E+06	8624
BDE-47	Air	1.61E+04	1	8.07E+03	1	5.31E+05	47	5.63E+05	50	1.12E+06	11467
	Water	5.19E+02	0	6.75E+04	1	1.71E+04	0	4.71E+06	98	4.79E+06	49169
	Soil	1.63E+00	0	9.41E+01	0	1.21E+06	99	6.56E+03	1	1.22E+06	12518
	All three	5.54E+03	0	2.52E+04	1	5.87E+05	25	1.76E+06	74	2.38E+06	24385

Based on Table 4.15, the environmental mass distribution of compounds was plotted regarding several media under different emission scenarios in Figure 4.26.

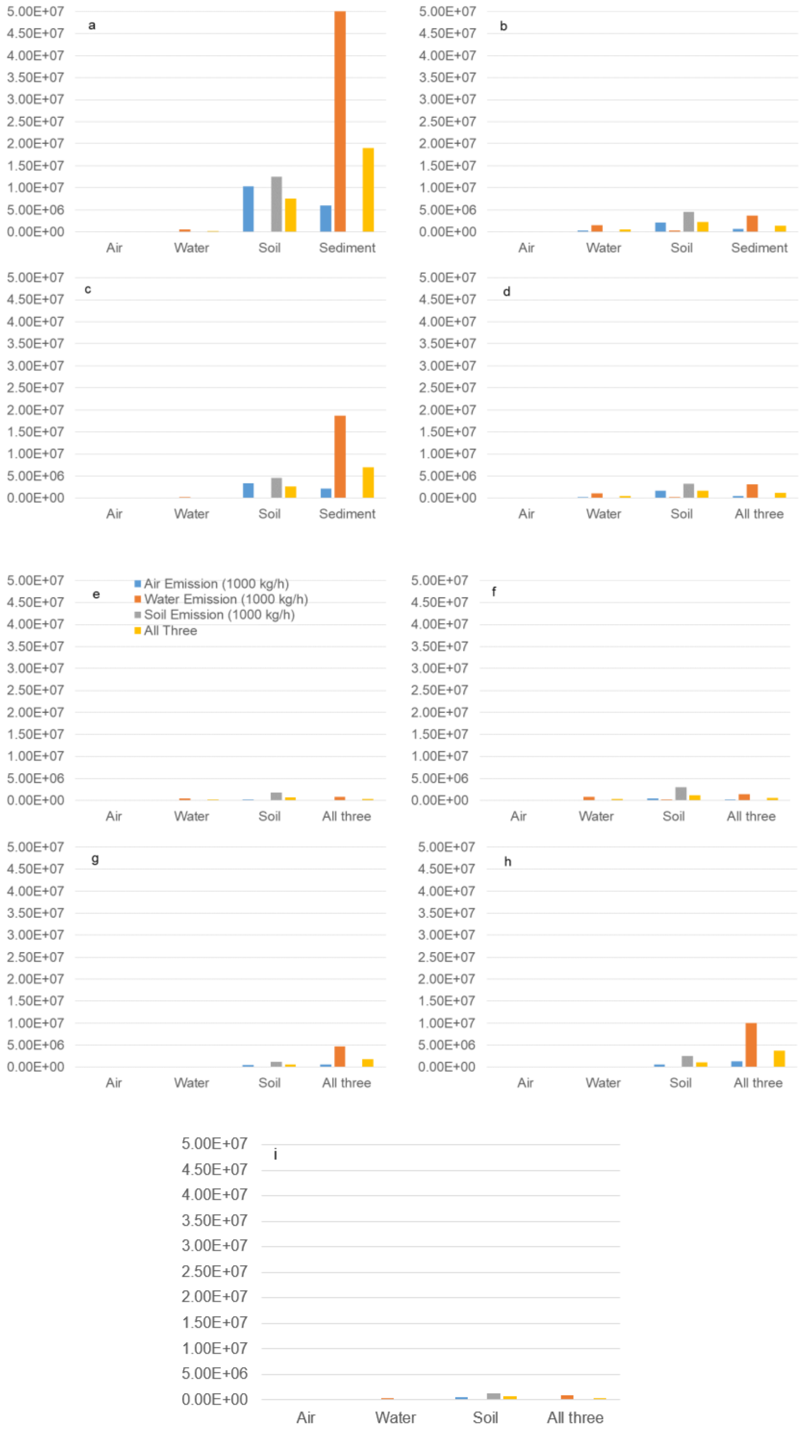


Figure 4.26. Amount (kg) of (a) BDE-153, (b) BDE-101, (c) BDE-99, (d) BDE-118, (e) BDE-52, (f) BDE-49, (g) BDE-47, (h) BDE-66, (i) BDE-77.

The persistence of BDEs, i.e. the amount that remains as steady-state, is seen to be the highest when BDEs are introduced into the environment via the water phase, because they accumulate in sediments. Although persistence of BDEs as can be seen from the last column of Table 4.15 does not show great variation when soil is the mode-of-entry, the amounts that remain in steady-state in the environment change because of differences in K_{oc}. The congeners that remain to a larger extent in the environment as indicated by the visible high bars in Figure 4.26 are BDE-153 and 99. Even though a relatively smaller amount of the other congeners are left in the environment, their persistence is not much lower when compared to BDE-153 and 99.

Individual persistence of BDE-153 and its TPs, along with their joint persistence, are demonstrated in Figure 4.27. Although the individual persistence of each PBDE congener is similar to BDE-153, due to factoring in the fraction of formation, secondary persistence of each congener is lower when compared to BDE-153. As is apparent from the figure, the persistence of BDE-153 is increased markedly if all degradation products are taken into consideration. Since BDE-153 may lead to many lower brominated TPs in the environment, its joint persistence is increased considerably. This result points to the ongoing effect of such contaminants in the environment. Even though their concentration can be reduced by degradation mechanisms, the many TPs produced will continue to persist in the environment.

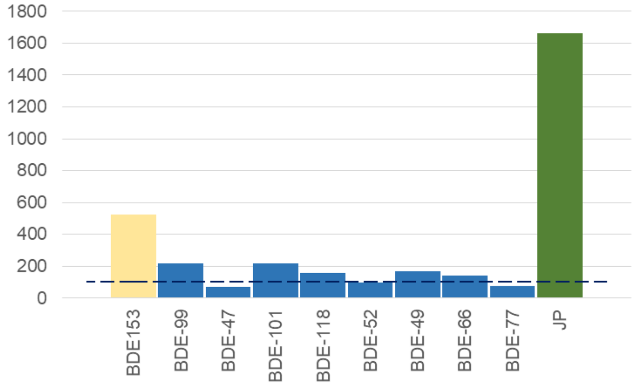


Figure 4.27. Persistence of BDE-153 family with a dashed line that is overall persistence criterion (P_{ov}) of 100 days (Webster et al., 1998).

The predictive capability of EPI Suite and the effects of physicochemical inputs on chemical amount and persistence is presented in Table 4.16. The percentage differences between EPI Suite predicted and FAVs for melting point, vapor pressure, solubility, K_H, log$K_{ow,}$ and K_{oc} as two orders of magnitude, but these differences do not generate a considerable effect on chemical amount and persistence excluding vapor pressure.

One order of magnitude reduction in VP of BDE-153 results in a significant decrease in persistence. This situation is similar to the surprising results obtained for some of the other previously studied compounds. When VP gets too small (i.e. less than 10^{-7} Pa), the EQC model most probably handles the compound as Type 2 (nonvolatile) and used the aquivalence approach (Mackay et al., 1996b), rather than use of fugacities. This approach results in zero partitioning into the air phase, i.e. zero percent as well as zero kg in air. Even though BDE-153 does not partition appreciably into air, even a small mass in air has an impact on the P_{ov}. This is because typically atmospheric half-lives are much smaller than half-lives in other media (e.g. 1100 hrs in air when compared to 38900 hrs in sediment). Subsequently, an unexpected change in persistence is obtained. Such a change in persistence with respect to change in VP is not observed in the upcoming sensitivity study. We believe this unexpected change in persistence obtained here does not represent a real change in persistence of BDE-153, but rather a possible artifact of the EQC model. The table does not contain half-lives because they were already estimated using EPI Suite, due to lack of experimental data.

Table 4.16. FAV and EPI Suite predicted inputs on BDE-153 amount and persistence with percentage difference.

Chem	**FAV**	**EPI Suite Value**	**Diff. Btw Inputs as %**	**Chem Amount (mole)**	**Persistence (d)**	**Percent Diff (%)**
BDE-153				1.94E+07	522	
BDE-153meltpred	1.62E+02	1.97E+02	-22	1.94E+07	522	0
BDE-153vaporpred	9.46E-06	2.82E-07	97	1.06E+07	283	-84
BDE-153solubpred	2.57E-02	2.81E-03	89	1.94E+07	522	0
BDE-153Henrypred	2.37E-01	6.47E-02	73	1.94E+07	522	0
BDE-153logKowpred	7.48E+00	8.20E+00	-10	1.94E+07	521	0
BDE-153Kocpred	3.43E+06	3.55E+04	99	1.94E+07	520	0
BDE-153predicted				1.06E+07	283	-84

Sensitivity analysis for BDE-153 family is indicated in Figure 4.28. According to this figure, half-life in soil is the most sensitive parameter for all members. Half-life in sediment could also be expected as a sensitive parameter, but since much less amount of chemical partitions into the sediments when compared to soil, the model is not sensitive to that parameter.

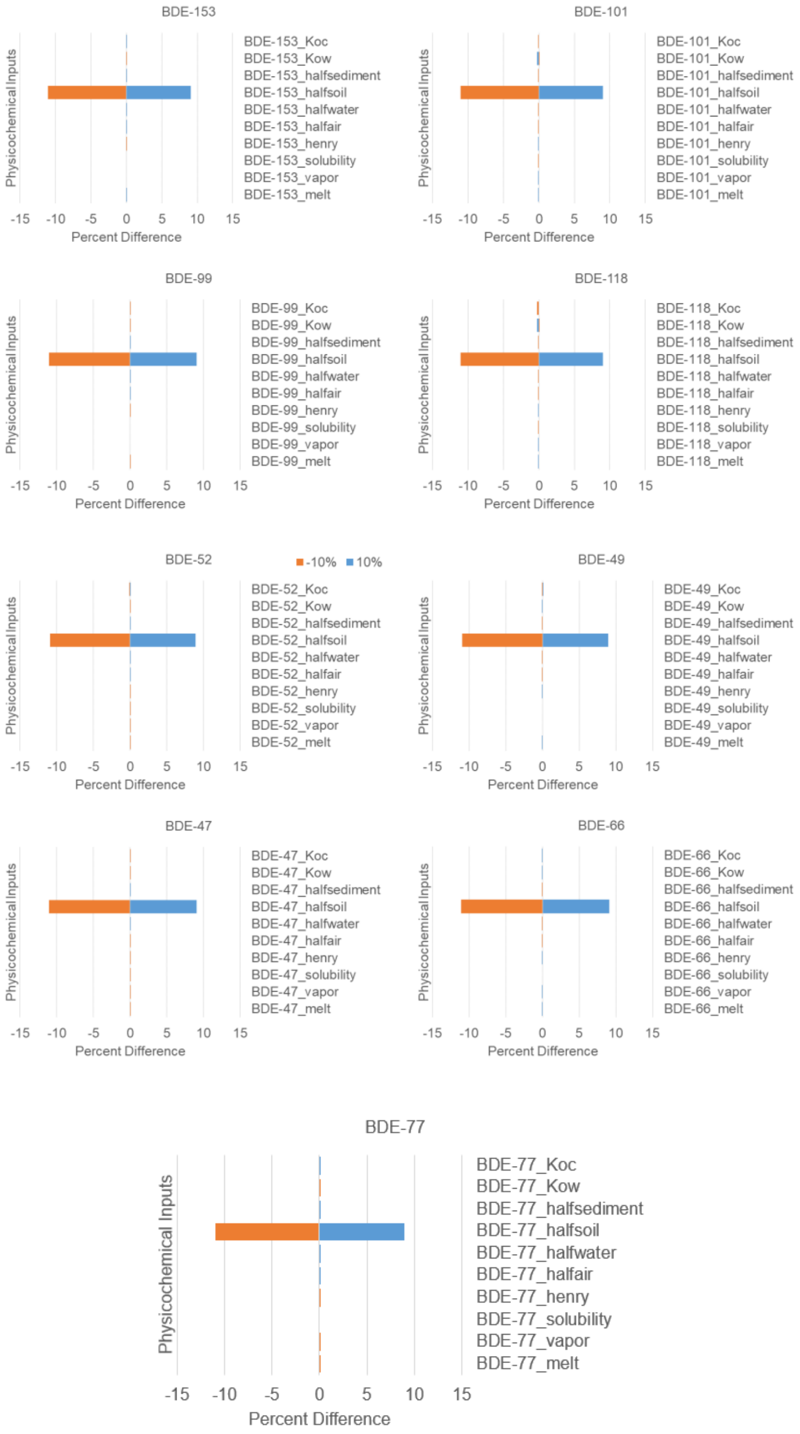


Figure 4.28. Sensitivity analysis result for BDE-153 and its TPs, namely, BDE-101, BDE-99, BDE-118, BDE-52, BDE-49, BDE-47, BDE-66, and BDE-77.

4.6 Diuron

Diuron is one of the phenylurea herbicides for controlling weeds in agricultural as well as non-agricultural fields. High pollution level is possible due to diuron persistence, so the EU limited its usage (Shankar et al., 2007). Common usage of diuron, its aqueous solubility, high persistency, and toxic intermediate formation lead to contamination of soil and aquatic ecosystems (Malato et al., 2003). While it has low acute toxicity via oral, inhalation, and dermal routes, it is labeled as a human carcinogen (USEPA, 2003).

4.6.1 Degradation Pathway Scheme for Diuron

Degradation scheme of diuron was directly taken from Gasser et al. (2007). Figure 4.29 shows the degradation scheme of diuron.

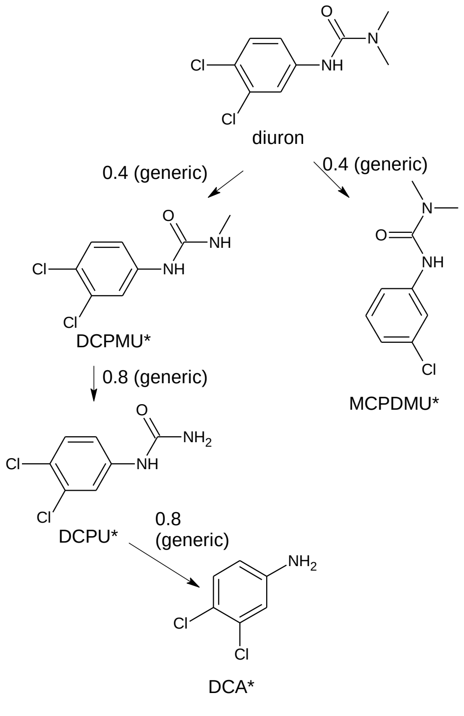


Figure 4.29. Degradation scheme of diuron (Gasser et al., 2007*). Number on each arrow indicates the fraction of formation of TPs.

4.6.2 Physicochemical Properties for Diuron Family

Compiled literature derived, EPI Suite predicted physicochemical property of parent chemical and TPs are presented in Appendix A-Table A1. FAV for parent chemical and its TPs are given in Appendix A- Table A2.

4.6.3 Evaluation and Persistency of Diuron Family

Table 4.17 shows the environmental mass distribution of the substance family, total mass, and persistence. For diuron, the main sink compartment is water and then soil. Soil and water run-off from soil to water could be mechanisms causing diuron accumulation in water medium. It does not reside in air and it is not likely to distribute into sediment. Unlike diuron, all TPs primarily distribute into soil medium and then water medium along with low amounts in sediment if we ignore the mode-of-entry effect.

Table 4.17. Amount of diuron & its TPs as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
Diuron	Air	0.00E+00	0	1.17E+06	60	7.80E+05	40	1.89E+03	0	1.95E+06	1951
	Water	0.00E+00	0	1.56E+06	100	0.00E+00	0	2.51E+03	0	1.56E+06	1562
	Soil	0.00E+00	0	1.13E+06	56	8.66E+05	43	1.82E+03	0	1.99E+06	1994
	All three	0.00E+00	0	1.28E+06	70	5.49E+05	30	2.07E+03	0	1.84E+06	1836
DCPMU	Air	1.72E+02	0	7.87E+04	8	8.69E+05	91	1.93E+03	0	9.49E+05	2374
	Water	2.39E-03	0	5.18E+05	98	1.20E+01	0	1.27E+04	2	5.31E+05	1327
	Soil	4.31E-02	0	3.09E+04	3	9.77E+05	97	7.57E+02	0	1.01E+06	2522
	All three	5.75E+01	0	2.09E+05	25	6.15E+05	74	5.12E+03	1	8.30E+05	2074
MCPDMU	Air	3.72E+02	0	8.89E+04	10	7.77E+05	90	1.29E+03	0	8.68E+05	2169
	Water	1.21E-02	0	5.19E+05	99	2.53E+01	0	7.56E+03	1	5.26E+05	1316
	Soil	3.41E-01	0	4.98E+04	5	9.39E+05	95	7.25E+02	0	9.90E+05	2474
	All three	1.24E+02	0	2.19E+05	28	5.72E+05	72	3.19E+03	0	7.95E+05	1986
DCPU	Air	8.55E+01	0	6.66E+04	9	6.92E+05	91	1.40E+03	0	7.60E+05	2375
	Water	7.33E-04	0	4.15E+05	98	5.93E+00	0	8.69E+03	2	4.23E+05	1323
	Soil	1.53E-02	0	2.85E+04	4	7.74E+05	96	5.97E+02	0	8.03E+05	2510
	All three	2.85E+01	0	1.70E+05	26	4.89E+05	74	3.56E+03	1	6.62E+05	2069
DCA	Air	4.03E+03	10	4.72E+03	12	3.00E+04	77	1.89E+02	0	3.89E+04	152
	Water	4.25E+01	0	3.28E+05	96	3.15E+02	0	1.31E+04	4	3.41E+05	1332
	Soil	3.20E+01	0	1.25E+04	2	6.35E+05	98	5.00E+02	0	6.48E+05	2531
	All three	1.37E+03	0	1.15E+05	34	2.22E+05	65	4.61E+03	1	3.43E+05	1338

Based on Table 4.17, the environmental mass of compounds was plotted considering various media under different emission scenarios in Figure 4.30. Mode-of-entry can be observed for emission into water medium regardless of the compounds.

No members of the diuron family accumulate in the air considerably when introduced into the air or any other media. When introduced air, soil or all media equally, all TPs accumulate appreciably in soil. Diuron, on the other hand always prefers the aqueous medium. It does not necessarily have the highest aqueous solubility, actually it has the lowest, but very low VP and comparatively higher half-life of diuron in water contribute to this outcome.

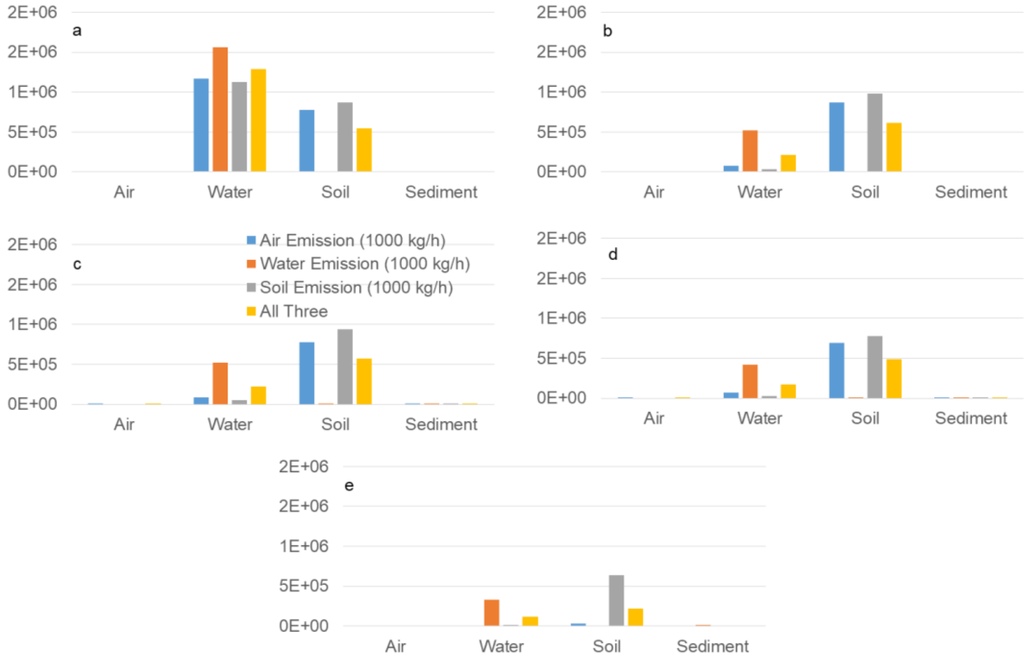


Figure 4.30. Amount (kg) of (a) diuron, (b) DCPMU, (c) MCPDMU, (d) DCPU and (e) DCA in the environment.

Individual persistence of diuron and its TPs, together with joint persistence, are showed in Figure 4.31. From this figure, the persistence of all TPs has less than the persistence of diuron. Also, as can be seen from Table 4.17, individual persistence of TPs are similar to each other. Despite less persistent TPs, diuron persistence would exceed threshold value substantially providing that TPs are considered in the persistence evaluation.

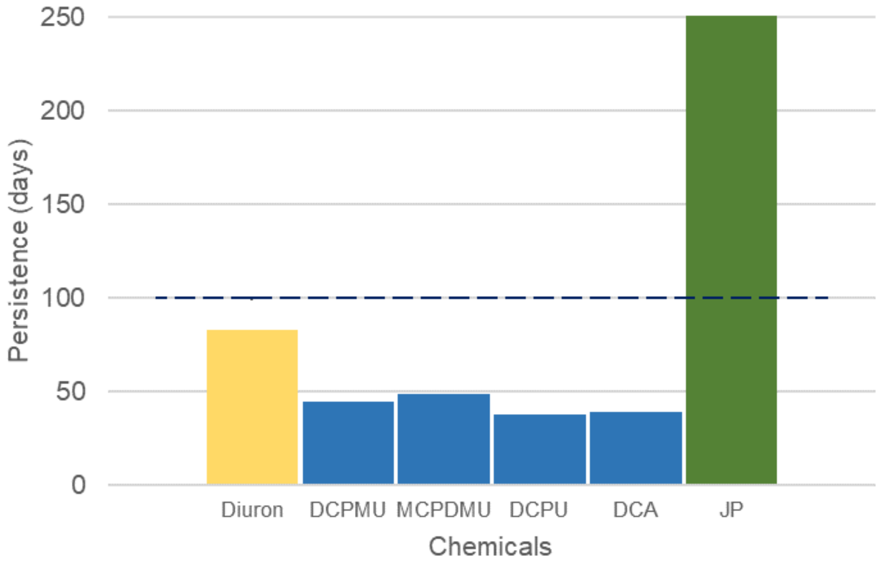


Figure 4.31. Persistence of diuron family with a dashed line that is P_{ov} criterion of 100 days (Webster et al., 1998).

The predictive capability of EPI Suite and the effects of physicochemical inputs on chemical amount and persistence is presented in Table 4.18. The percentage differences between EPI Suite predicted and FAVs for melting point, solubility, K_H, $\log K_{ow}$, and K_{oc} are two or three orders of magnitude, but they do not have any influence on chemical amount and persistence. Nonetheless, overpredicted vapor pressure generates two orders of magnitude change in percent difference for persistence and diuron mass.

Although differences between FAV and EPI Suite prediction for half-life in air and sediment are as three orders of magnitude, these differences could not generate any effect on diuron mass and persistence. On the other hand, FAV and EPI Suite predicted half-life in water and soil are different from each other as two orders of magnitude. As a result, percent differences for persistence and environmental mass are two and one order of magnitude, respectively. Overall, vapor pressure, half-life in water, and soil should be given priority in terms of obtaining experimental, diligently obtained data, as much as possible when compared to other physicochemical inputs.

Table 4.18. FAV and EPI Suite predicted inputs on diuron amount and persistence with percentage difference.

Chem	FAV	EPI Suite Value	Diff. Btw Inputs as %	Chem Amount (mole)	Persistence (d)	Percent Diff (%)
diuron				8.56E+06	83	
diuronmeltpred	1.58E+02	1.26E+02	20	8.56E+06	83	0
diuronvaporpred	9.97E-05	2.09E-04	-110	1.29E+07	125	34
diuronsolubpred	3.69E+01	3.03E+02	-721	8.56E+06	83	0
diuronHenrypred	6.30E-04	1.60E-04	75	8.56E+06	83	0
diuronairhalfpred	3.00E+00	2.40E+01	-700	8.56E+06	83	0
diuronwaterpred	1.08E+03	9.00E+02	17	7.74E+06	75	-11
diuronsoilpred	2.16E+03	1.80E+03	17	8.10E+06	79	-6
diuronsedpred	1.15E+03	8.10E+03	-603	8.56E+06	83	0
diuronlogKowpred	3.16E+00	2.72E+00	14	8.55E+06	83	0
diuronKocpred	3.98E+02	1.09E+02	73	8.55E+06	83	0
diuronpredicted				1.01E+07	98	16

The sensitivity analysis for the diuron family is demonstrated in Figure 4.32. According to this figure, half-life in soil is considerable for diuron. Notwithstanding, the other two parameters could be more sensitive than half-life in soil of diuron. For example, a ten percent increase in vapor pressure and a ten percent decrease in half-life in water have more importance in decreasing order. Also, ten percent increase in vapor pressure causes significant persistence increase while a ten percent decrease does not cause any change on persistence. Contrary to diuron, half-life in soil is the most sensitive parameter for all TPs.

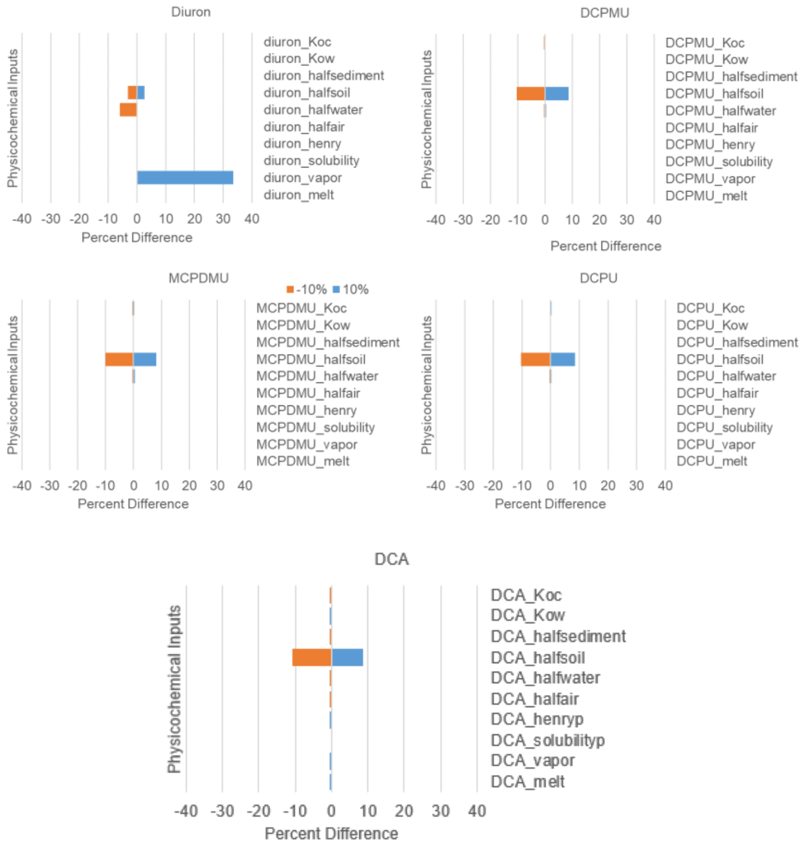


Figure 4.32. Sensitivity analysis for diuron, DCPMU, MCPDMU, DCPU, and DCA.

4.7 Alachlor

Alachlor, also known as 2-chloro-N-(2,6-diethylphenyl)-N-(methoxy-methyl) acetamide, is a herbicide that can accumulate in surface water and groundwater due to its moderate persistency characteristic and excessive usage (Graham et al., 1999). It is transported in surface waters and groundwater. According to USEPA, alachlor is likely to be a human carcinogen at high doses, not at low doses (USEPA, 1998b).

4.7.1 Degradation Pathway Scheme for Alachlor

Under natural conditions, alachlor oxanilic acid (alachlor OXA) and alachlor ethane sulfonic acid (alachlor ESA) can occur in surface water (Graham et al., 1999). Even though alachlor demonstrates high stability in water in case of natural sunlight irradiation, photocatalysis usage namely, $FeCl_3$, or TiO_2 accelerates degradation (Peñuela & Barceló, 1996). Photolysis can be promoted by adding heterogeneous TiO_2 catalysis with H_2O_2 or $Na_2S_2O_8$ (Pérez et al., 2018). Also, photolysis and photocatalysis treatment result in lactam and alachlor OXA formation (Peñuela & Barceló, 1996; Pérez et al., 2018). Figure 4.33 indicates the degradation scheme of alachlor.

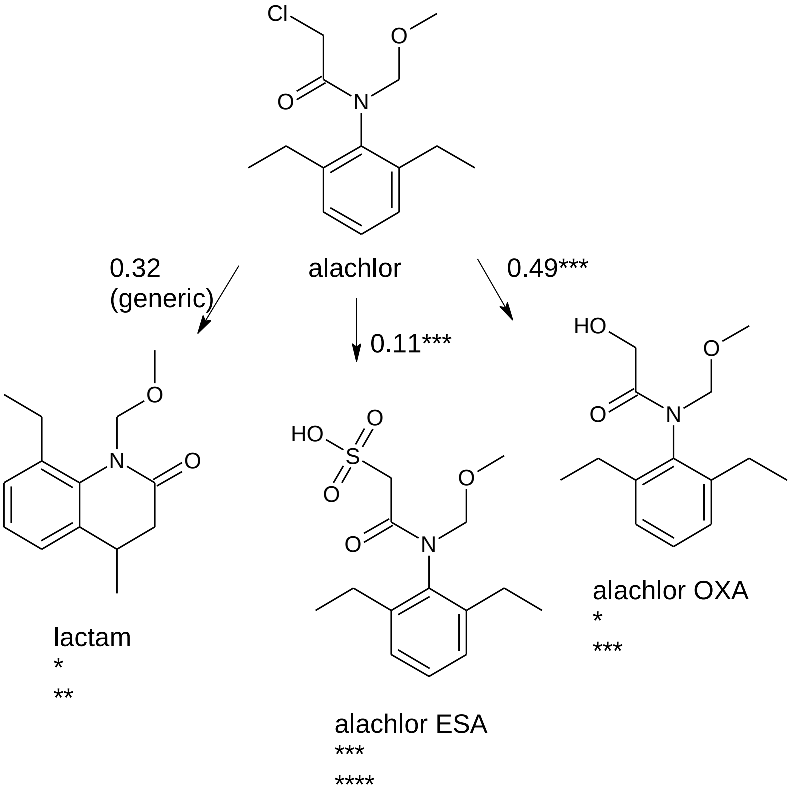


Figure 4.33. Degradation scheme of alachlor (Gasser et al., 2007****; Graham et al., 1999***; Peñuela & Barceló, 1996**; Pérez et al., 2018*). Number on each arrow indicates the fraction of formation of TPs from the parent compound.

4.7.2 Physicochemical Properties for Alachlor Family

Compiled literature derived physicochemical property of parent chemical and EPI Suite predicted TPs are presented in Appendix A-Table A1. FAVs for the parent chemical and their TPs are given in Appendix A-Table A2.

4.7.3 Evaluation and Persistency of Alachlor Family

Table 4.19 shows the environmental mass distribution of the substance family, total mass, and persistence. For alachlor, soil or water is the most dominant sink depending on the emission scenario. Alachlor and lactam are more likely to be transported from soil to air via diffusion, when compared to the other two members of the family. On the other hand, run-off from soil to water is a considerable intermedia transport mechanism for alachlor ESA and OXA. Negligible amounts of alachlor can be observed in air and sediment media. Like alachlor, the dominant sink for lactam and alachlor OXA can change with respect to the emission scenario. Excluding alachlor ESA amount in air compartment, low amounts of TPs are valid in air and sediment media.

Table 4.19. Amount of alachlor & its TPs as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
Alachlor	Air	5.90E+03	2	6.71E+04	18	2.99E+05	80	2.79E+01	0	3.72E+05	372
	Water	1.04E+00	0	7.93E+05	100	5.29E+01	0	3.29E+02	0	7.93E+05	793
	Soil	1.10E+01	0	2.39E+04	5	5.03E+05	95	9.94E+00	0	5.27E+05	527
	All three	1.97E+03	0	2.95E+05	52	2.67E+05	47	1.22E+02	0	5.64E+05	564
Lactam	Air	8.23E+02	0	7.77E+04	17	3.79E+05	83	4.90E+02	0	4.58E+05	1425
	Water	1.07E-01	0	4.17E+05	99	4.94E+01	0	2.63E+03	1	4.20E+05	1306
	Soil	5.79E+00	0	8.81E+04	12	6.57E+05	88	5.55E+02	0	7.46E+05	2318
	All three	2.76E+02	0	1.94E+05	36	3.45E+05	64	1.22E+03	0	5.41E+05	1683
Alachlor ESA	Air	0.00E+00	0	1.01E+05	56	8.03E+04	44	1.95E+02	0	1.81E+05	1670
	Water	0.00E+00	0	1.41E+05	100	0.00E+00	0	2.73E+02	0	1.41E+05	1301
	Soil	0.00E+00	0	9.65E+04	52	8.92E+04	48	1.87E+02	0	1.86E+05	1711
	All three	0.00E+00	0	1.13E+05	67	5.65E+04	33	2.18E+02	0	1.70E+05	1560
Alachlor OXA	Air	4.46E+01	0	3.86E+05	44	4.85E+05	56	8.89E+02	0	8.71E+05	1780
	Water	1.26E-04	0	6.35E+05	100	1.37E+00	0	1.46E+03	0	6.37E+05	1301
	Soil	2.22E-02	0	3.63E+05	40	5.45E+05	60	8.37E+02	0	9.09E+05	1857
	All three	1.49E+01	0	4.61E+05	57	3.43E+05	43	1.06E+03	0	8.05E+05	1646

Based on Table 4.19, the environmental mass of compounds was plotted regarding several media under different emission scenarios in Figure 4.34. Alachlor emission into only water and alachlor emission into only soil causes the highest amount in water and soil, respectively. On the other hand, emission to air could not cause the highest amount in the air phase. Although alachlor has a high solubility, its log K_{ow} which is not very small results in appreciable accumulation onto soil when introduced into the air, soil, or all three media equally.

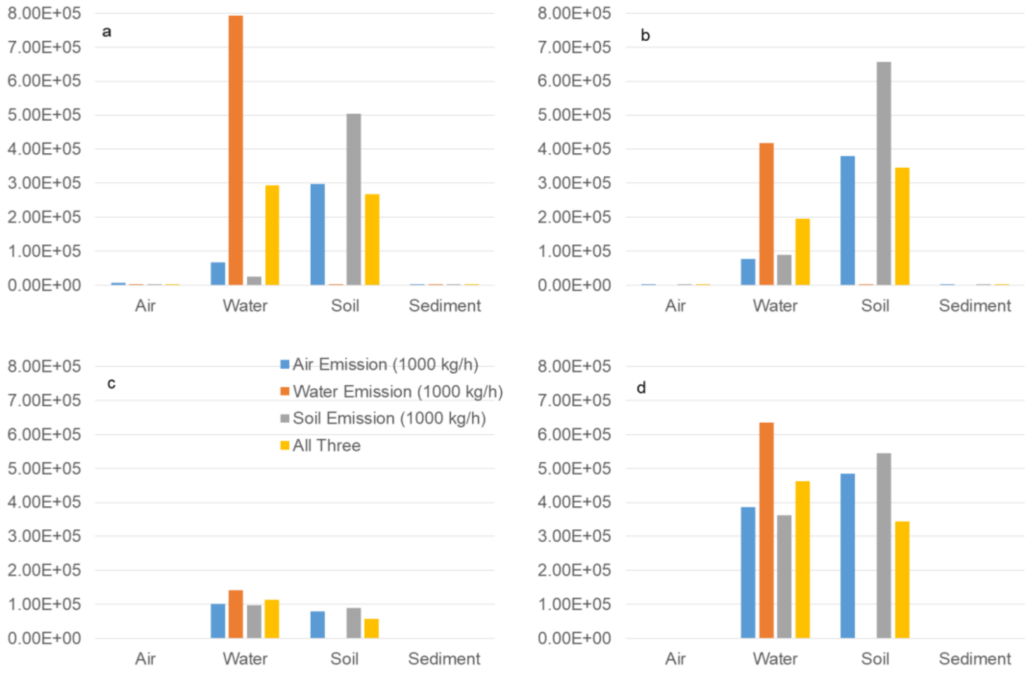


Figure 4.34. Amount (kg) of the (a) alachlor, (b) lactam, (c) alachlor ESA, and (d) alachlor OXA in the environment.

The individual persistence of alachlor and its TPs, together with their JP, is demonstrated in Figure 4.35. As can be seen from this figure, the persistence of alachlor is increased remarkably if degradation products are considered. Persistence of degradation products could be less, or higher than alachlor. For this family, lactam, and alachlor OXA have higher persistence contribution to joint persistence, but alachlor ESA has less owing to its low fraction of formation from the parent alachlor.

In brief, the JP of the family is three times more than the primary persistence. Besides, joint persistence exceeds the overall persistence threshold that was stated as 100 days by Webster et al. (1998). In addition to alachlor monitoring, lactam and alachlor OXA should be monitored especially in aqueous media for comprehensive persistence assessment of alachlor.

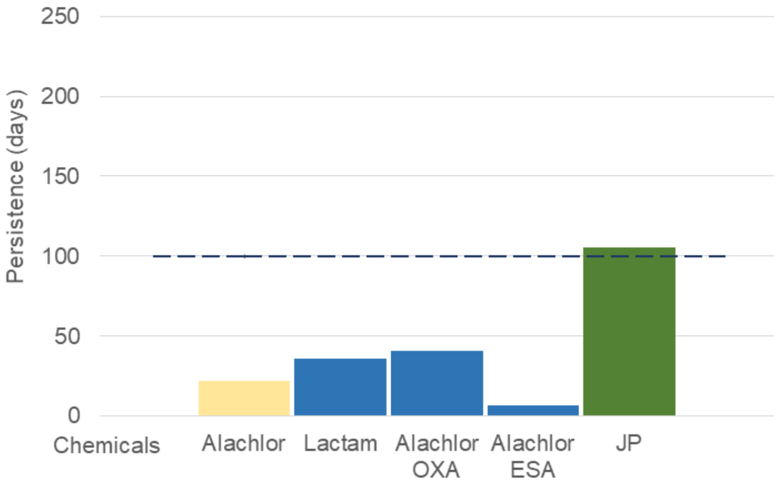


Figure 4.35. Persistence of alachlor family with a dashed line that is P_{ov} criterion of 100 days (Webster et al., 1998).

The predictive capability of EPI Suite and the effects of physicochemical inputs on chemical amount and persistence can be analyzed in Table 4.20. Even though differences between FAV and EPI Suite prediction for melting point, vapor pressure, solubility, K_H, and $\log K_{ow}$ are valid, these differences could not generate any effect on chemical amount and persistence. Furthermore, the percentage difference between EPI Suite predicted and FAVs for K_{oc} as two orders of magnitude, but this difference generates one order of magnitude change in percent difference for chemical amount and persistence. Final adjusted and EPI Suite predicted half-life in water and soil are different from each other as three orders of magnitude in percentage. As a result, differences in persistence are as one and two orders of magnitude, respectively. However, two orders of magnitude difference in air half-life and five orders of magnitude in sediment do not create any deviation on chemical concentration and persistence. This is mainly because alachlor does not accumulate in air or sediment appreciably, as can be seen from Table 4.19. Overall, half-life in soil, water, and K_{oc} has decreasing order significance within physicochemical parameters and they should be determined correctly as much as possible.

Table 4.20. Effect of FAV and EPI Suite predicted inputs on alachlor amount and persistence with percentage difference.

Input Data	FAV	EPI Suite Value	Diff. Btw Inputs as (%)	Chem Amount (mole)	Persistence (d)	Percent Diff. Btw Outputs(%)
alachlor				1.96E+06	22	
alachlormeltpred	4.00E+01	1.28E+02	-220	1.96E+06	22	0
alachlorvaporpred	1.99E-03	3.03E-03	-52	1.96E+06	22	0
alachlorsolubpred	2.42E+02	4.01E+02	-66	1.96E+06	22	0
alachlorHenrypred	2.22E-03	2.04E-03	8	1.96E+06	22	0
alachlorairhalfpred	1.20E+01	6.00E+00	50	1.95E+06	22	0
alachlorwaterpred	5.52E+02	1.44E+03	-161	2.10E+06	24	7
alachlorsoilpred	3.60E+02	2.88E+03	-700	1.29E+07	145	85
alachlorsedpred	4.80E+01	1.30E+04	-26983	1.96E+06	22	0
alachlorlogKowpred	2.99E+00	3.60E+00	-20	1.96E+06	22	0
alachlorKocpred	1.62E+02	3.12E+02	-93	1.94E+06	22	-1
alachlorpredicted				1.45E+07	163	86

The sensitivity analysis for the alachlor family is demonstrated in Figure 4.36. It can be apparently seen from this figure, half-life in soil is the most sensitive parameter for alachlor, lactam, and alachlor OXA. Half-life in water is the most sensitive parameter for alachlor ESA. This is consistent with the fact that alachlor ESA has a much greater presence when compared to the other TPs in water phase when soil is the mode of entry. Additionally, K_{oc} might gain significance as alachlor transforms into lactam and alachlor OXA.

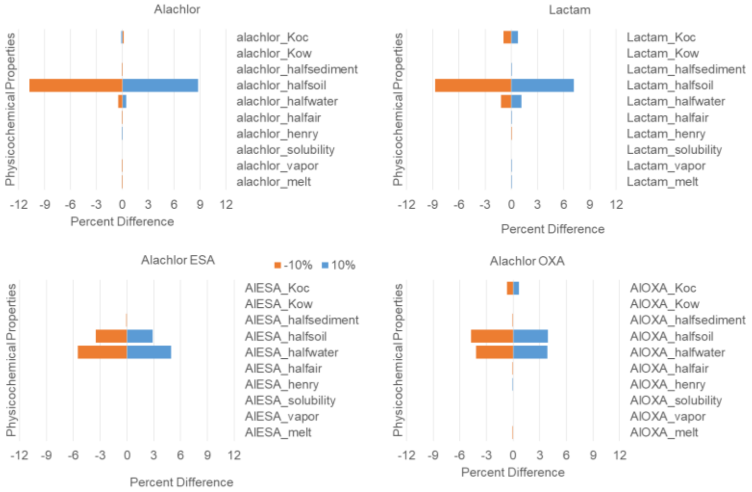


Figure 4.36. Sensitivity analysis results for alachlor and its TPs, namely, lactam, alachlor ESA, and alachlor OXA.

4.8 Trifluralin

Trifluralin (2,6-dinitro-N, N-dipropyl-4-(trifluoromethyl)-benzenamine) is a commonly used dinitroaniline herbicide for grasses and weeds (Klupinski & Chin, 2003). USEPA (1996) reported it to be immobile and fairly persistent in soils that are rich in microorganisms. Trifluralin was labeled as practically nontoxic for acute oral toxicity and dermal irritation, while listed as slightly toxic for acute inhalation, and eye irritation potential. Also, it was placed in group C as it is a possible human carcinogen. Hence, understanding the environmental fate of trifluralin and its TPs formation is important to better evaluate their effects on the ecosystem and public health (Gong et al., 2016).

4.8.1 Degradation Pathway Scheme for Trifluralin

Abiotic degradation of trifluralin was investigated under mimicked wetland sediment conditions (Klupinski & Chin, 2003). In the study, Fe (II)/goethite suspension was supplied as it is likely to be present in anoxic wetland sediments. Surface-mediated abiotic degradation was shown as a mechanism to degrade trifluralin. They report

TR-7 and TR-9 as two of the final products. Even though TR-4 is one of the intermediate compounds, it was included in the degradation pathway, since its degradation gives the same TPs that result from trifluralin degradation. All observed TPs were detected in soil and sediment media (Klupinski & Chin, 2003). Figure 4.37 demonstrates the degradation scheme of trifluralin.

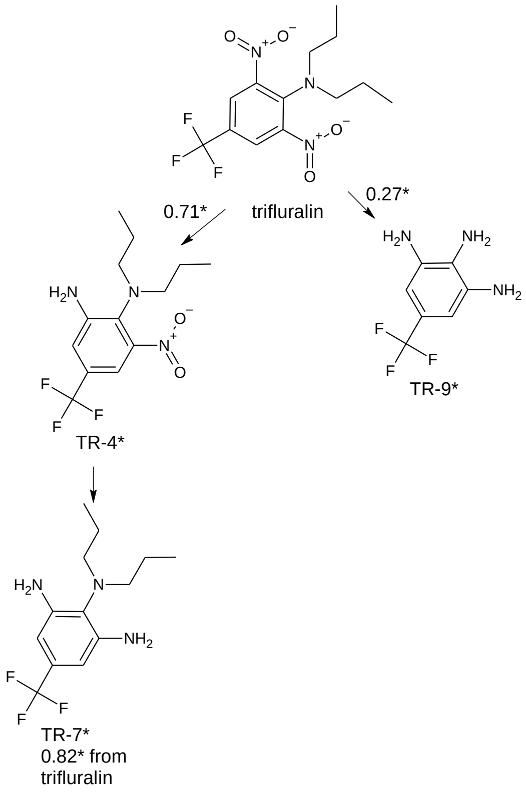


Figure 4.37. Degradation scheme of trifluralin (Klupinski & Chin, 2003*) with the ff^{xy} values.

4.8.2 Physicochemical Properties for Trifluralin Family

Compiled literature derived physicochemical property of parent chemical and EPI Suite predicted TPs are presented in Appendix A-Table A1. FAVs for parent chemical and its TPs are given in Appendix A- Table A2.

4.8.3 Evaluation and Persistency of Trifluralin Family

Table 4.21 indicates the environmental mass distribution of the substance family, total mass, and persistence. It is apparent from the table that trifluralin is a multi-media compound capable of being accumulated in various media such as air (44%), water (43%), soil (almost 100%), and sediment (50%) depending on different modes of entry. Water & soil and soil & water are the first and second sink media for TR-7 and TR-9, respectively. While low amounts of trifluralin, TR-4, and TR-9 could be determined in air medium, TR-7 cannot be detected in the air medium. The high presence of TR-7 in aqueous medium regardless of mode-of-entry stems from low VP and resulting very low K_{aw}. Non-equilibrium accumulation in water phase indicates slow intermedia transfer from the water to sediment.

Table 4.21. Amount of trifluralin & its TPs as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
Trifluralin	Air	2.24E+05	44	8.72E+04	17	9.44E+04	19	1.01E+05	20	5.06E+05	506
	Water	1.07E+05	5	9.89E+05	43	4.49E+04	2	1.14E+06	50	2.28E+06	2282
	Soil	4.47E+02	0	1.44E+03	0	2.45E+06	100	1.66E+03	0	2.45E+06	2450
	All three	1.10E+05	6	3.59E+05	21	8.62E+05	49	4.14E+05	24	1.75E+06	1746
TR-4	Air	8.62E+03	1	7.62E+04	7	9.96E+05	85	8.62E+04	7	1.17E+06	1651
	Water	1.43E+02	0	3.85E+06	47	1.65E+04	0	4.36E+06	53	8.22E+06	11638
	Soil	2.91E+01	0	7.20E+04	1	8.62E+06	98	8.16E+04	1	8.78E+06	12419
	All three	2.93E+03	0	1.33E+06	22	3.21E+06	53	1.51E+06	25	6.05E+06	8569
TR-7	Air	0.00E+00	0	4.68E+06	85	8.03E+05	15	9.30E+03	0	5.49E+06	6736
	Water	0.00E+00	0	5.08E+06	100	0.00E+00	0	1.01E+04	0	5.09E+06	6245
	Soil	0.00E+00	0	4.64E+06	84	8.93E+05	16	9.21E+03	0	5.54E+06	6791
	All three	0.00E+00	0	4.80E+06	89	5.65E+05	11	9.53E+03	0	5.37E+06	6591
TR-9	Air	6.33E+00	0	9.11E+04	9	9.32E+05	91	3.39E+03	0	1.03E+06	3778
	Water	7.52E-06	0	5.62E+05	96	1.11E+00	0	2.09E+04	4	5.83E+05	2146
	Soil	1.03E-04	0	4.01E+04	4	1.05E+06	96	1.49E+03	0	1.09E+06	4013
	All three	2.11E+00	0	2.31E+05	26	6.60E+05	73	8.59E+03	1	9.00E+05	3312

Based on this table, the environmental mass of compounds was plotted regarding various media under several emission scenarios in Figure 4.38. Trifluralin, TR-4 and TR-9 amounts in soil could be affected from emission to soil medium. Dominance in water medium for TR-7 indicates limited intermedia transfer from water to other phases.

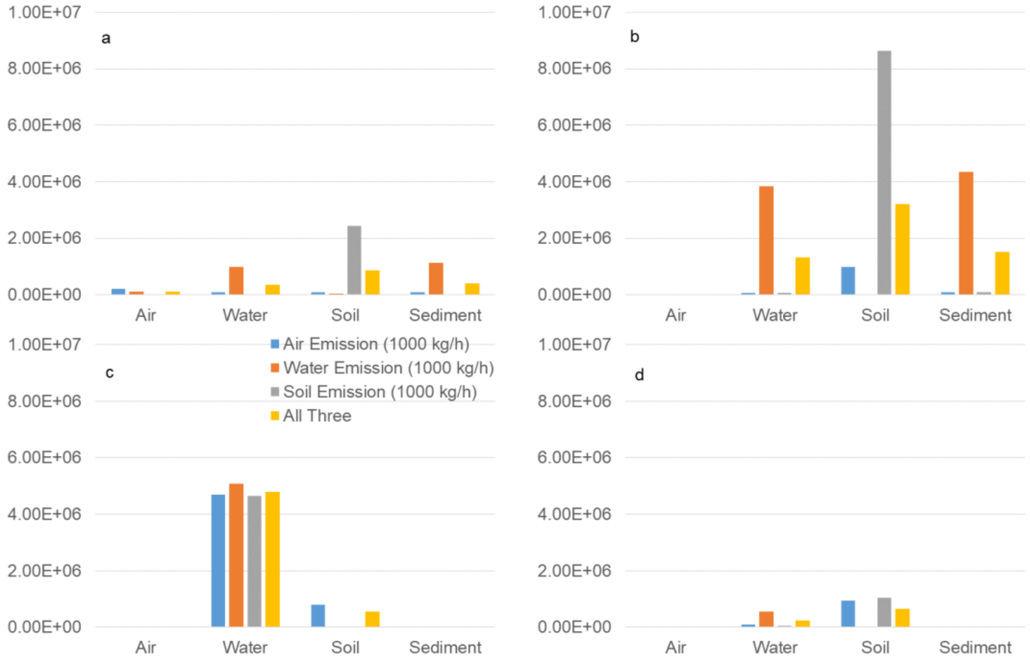


Figure 4.38. Amount (kg) of (a) trifluralin, (b) TR-4, (c) TR-7, and (d) TR-9 in the environment.

The individual persistence of trifluralin and its TPs are represented in Figure 4.39. As is apparent from this figure, the persistence of trifluralin is increased significantly when degradation products are regarded. Especially the greater half-lives of TR-4 and TR-7 in water and soil results in higher persistence of these compounds. For example, they are five times more resistant to degradation in soil and 2.5 times more resistant to degradation in water (Table A-1 in Appendix). TR-4 and TR-7 have a higher contribution to joint persistence compared to trifluralin and TR-9. Their higher individual persistence can be seen in the last column of Table 4.21. TR-9 has the least contribution to JP. To be brief, joint persistence is eight times more than the threshold value and primary persistence. TR-4 and TR-7 should be monitored along with trifluralin because of their high persistence contribution to JP.

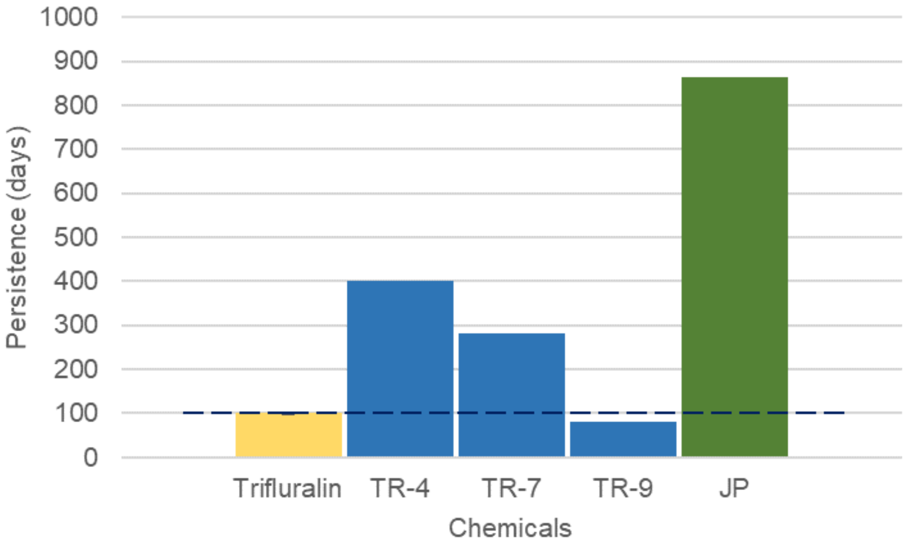


Figure 4.39. Persistence of trifluralin family with a dashed line that is overall persistence criterion (P_{ov}) of 100 days (Webster et al., 1998).

The predictive capability of EPI Suite and the effects of physicochemical inputs on chemical amount and persistence can be understood from Table 4.22. The percentage difference between EPI Suite predicted and FAV for melting point, vapor pressure, solubility, and partitioning coefficients can change from one to three orders of magnitude. However, these differences do not change the chemical amount and persistence. Only three orders of magnitude in soil half-life cause two orders of magnitude change in percent difference in chemical concentration and persistence. Hence, experimental work on factors affecting soil half-life and a more comprehensive determination of soil half-life for trifluralin would be useful.

The sensitivity analysis for the trifluralin family is represented in Figure 4.40. Based on this figure, while half-life in soil is the most sensitive parameter for trifluralin, TR-4, and TR-9, half-life in water is the most sensitive parameter for TR-7. Further, a ten percent decrease in vapor pressure of TR-4 leads to remarkable persistence change, and this change is more effective than a ten percent decrease in soil half-life.

Table 4.22. Effect of FAV and EPI Suite predicted inputs on trifluralin amount and persistence with percentage difference.

Chem	FAV	EPI Suite Value	Diff. Btw Inputs as %	Chem Amount (mole)	Persistence (d)	Percent Diff (%)
trifluralin				7.31E+06	102	
trifluralinmeltpred	4.90E+01	1.40E+02	-186	7.31E+06	102	0
trifluralinvaporpred	1.60E-02	2.25E-03	86	7.31E+06	102	0
trifluralinsolubpred	8.15E-01	4.39E-02	95	7.31E+06	102	0
trifluralinHenrypred	6.56E+00	1.72E+01	-162	7.29E+06	102	0
trifluralinairhalfpred	1.70E+02	1.10E+01	94	7.31E+06	102	0
trifluralinwaterpred	1.70E+03	4.32E+03	-154	7.31E+06	102	0
trifluralinsoilpred	1.70E+03	8.64E+03	-408	3.67E+07	513	80
trifluralinsedpred	5.50E+03	3.89E+04	-607	7.32E+06	102	0
trifluralinlogKowpred	5.17E+00	5.33E+00	-3	7.31E+06	102	0
trifluralinKocpred	2.34E+04	1.64E+04	30	7.30E+06	102	0
trifluralinpredicted				3.61E+07	504	80

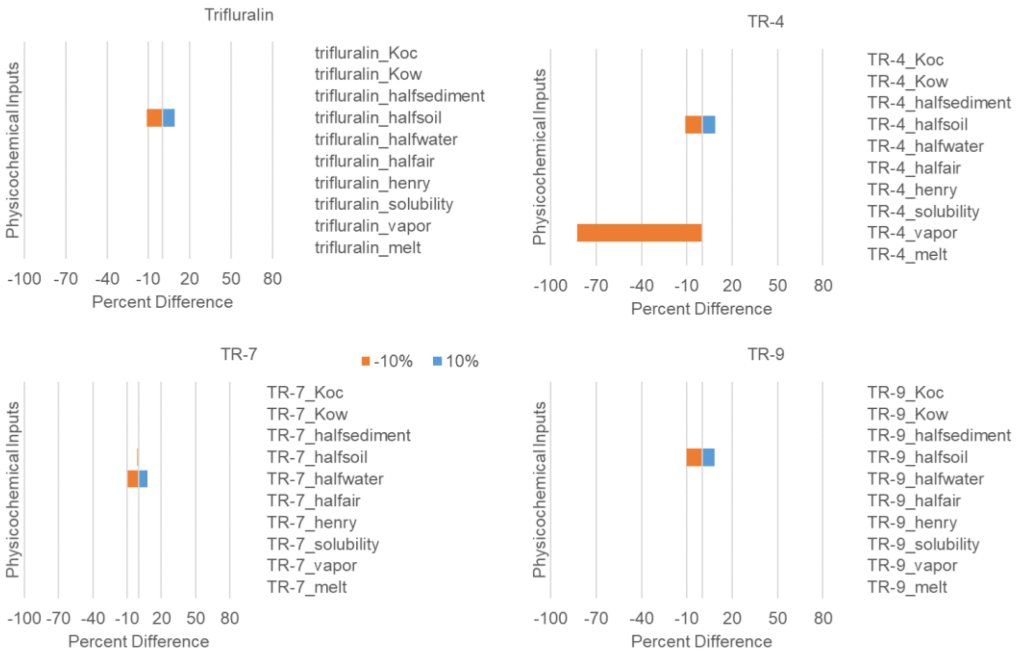


Figure 4.40. Sensitivity analysis for trifluralin and its TPs, namely, TR-4, TR-7, and TR-9.

4.9 Chlorpyrifos (CP)

CP, O, O-diethyl O-(3, 5,6-trichloro-2-pyridyl phosphorothioate, with the trade name chlorpyrifos is one of the widespread used organophosphate pesticides (OP) for crops in the last three decades (Supreeth & Raju, 2017). This insecticide is effective against several insect pests. Chlorpyrifos has long-range transportability in the atmosphere (Giesy et al., 2014). In spite of its restricted application in various countries, many developing countries continue to use chlorpyrifos due to its low cost (John & Shaike, 2015). It is moderately toxic with respect to acute oral, inhalation, and dermal toxicity. Like animals, humans are susceptible to acute and short term oral/dermal chlorpyrifos exposure (USEPA, 2000).

4.9.1 Degradation Pathway Scheme for Chlorpyrifos

In the case of free chlorine contact, CP could quickly oxidize to chlorpyrifos oxon (CPO) that has more toxic properties as compared to CP (Duirk & Collette, 2006) CP can directly turn into 3,5,6-trichloro-2-pyridinol (TCP) or formed CPO could hydrolyze into TCP. Since oxidation and hydrolysis can be commonly observed in the disinfection process, CPO and TCP are probable two dangerous TPs from CP in a water medium (Duirk & Collette, 2006). Furthermore, CPO and TCP could be formed via biotransformation including either oxidation or hydrolysis mechanisms (Supreeth & Raju, 2017). Figure 4.41 indicates the degradation scheme of chlorpyrifos.

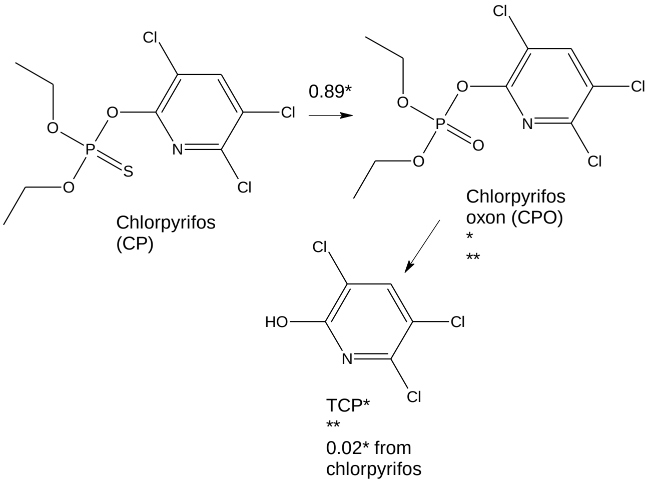


Figure 4.41. Degradation scheme of chlorpyrifos (Duirk & Collette, 2006*; Supreeth & Raju, 2017**) with the fraction of formation.

4.9.2 Physicochemical Properties for Chlorpyrifos Family

Compiled literature derived physicochemical property of parent chemical and EPI Suite predicted TPs are presented in Appendix A-Table A1. FAVs for parent chemical and its TPs are given in Appendix A- Table A2.

4.9.3 Evaluation and Persistency of Chlorpyrifos Family

Table 4.23 shows the environmental mass distribution of the substance family, total mass, and persistence. Excluding emission into only water medium, the soil is the dominant environmental compartment for chlorpyrifos. CP does not tend to reside in air or sediment media. For CPO and TCP, low amounts in the air might indicate high deposition from air to other media, especially to soil. Like CP, CPO and TCP are likely to accumulate in soil when introduced into soil. Compared CPO to other chemicals considered in this study, CP family has a higher tendency to accumulate in water.

Table 4.23. Amount of chlorpyrifos & its TPs as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
CP	Air	8.97E+03	31	4.39E+03	15	1.50E+04	53	1.75E+02	1	2.85E+04	29
	Water	4.14E+02	0	7.63E+05	96	6.93E+02	0	3.05E+04	4	7.94E+05	794
	Soil	5.55E+00	0	1.44E+03	0	1.04E+06	100	5.77E+01	0	1.04E+06	1038
	All three	3.13E+03	1	2.56E+05	41	3.51E+05	57	1.02E+04	2	1.86E+06	620
CPO	Air	1.04E+03	0	3.28E+05	11	2.59E+06	89	6.91E+03	0	2.93E+06	3287
	Water	7.11E-02	0	1.85E+06	98	1.77E+02	0	3.89E+04	2	1.89E+06	2117
	Soil	1.46E+00	0	2.10E+05	6	3.28E+06	94	4.42E+03	0	3.50E+06	3924
	All three	3.48E+02	0	7.95E+05	29	1.96E+06	71	1.67E+04	1	8.31E+06	3109
TCP	Air	5.86E+02	1	6.55E+03	10	5.62E+04	88	1.87E+02	0	6.36E+04	3739
	Water	1.13E+00	0	3.52E+04	97	1.09E+02	0	1.01E+03	3	3.63E+04	2134
	Soil	6.76E+00	0	3.14E+03	5	6.43E+04	95	8.98E+01	0	6.76E+04	3975
	All three	1.98E+02	0	1.49E+04	27	4.02E+04	72	4.28E+02	1	1.67E+05	3283

Based on Table 4.23, the environmental mass of compounds was plotted regarding several media under various emission scenarios in Figure 4.42. As is evident from the comparison of Figure 4.42 panels a, b, and c, CP, with a fraction of 0.89 degraded and transformed into CPO, while TCP is transformed to a much smaller extent with ff of 0.02 (Figure 4.41). Since CPO is much more resistant to degradation, more of this compound ends up accumulating in soil or water media, depending on mode-of-entry.

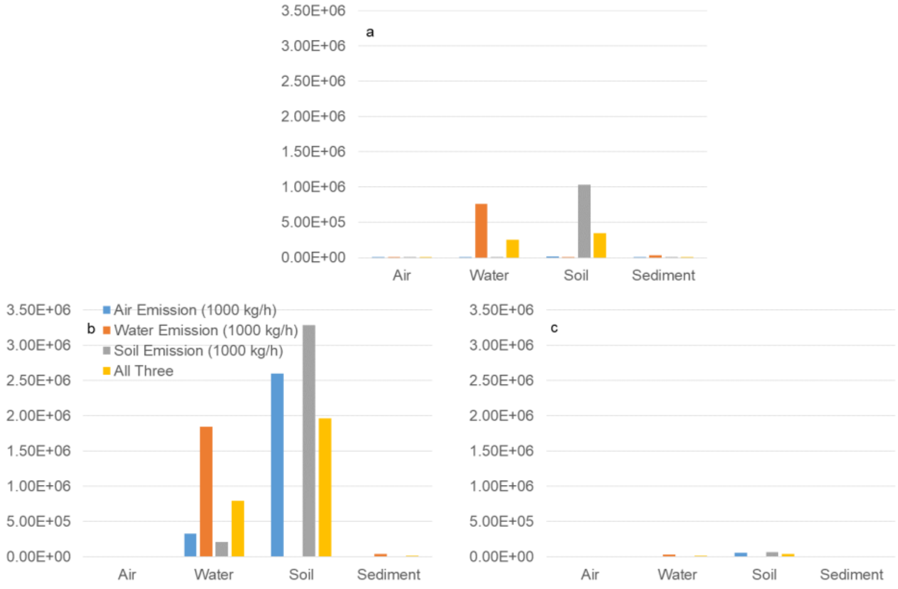


Figure 4.42. Amount (kg) of (a) chlorpyrifos, (b) chlorpyrifos oxon, and (c) TCP in the environment.

Regardless of the compound, the highest amount of any member in the water and soil medium is due to mode-of-entry into water and soil, respectively. Individual persistence of chlorpyrifos and its TPs, together with their joint persistence are represented in Figure 4.43. As is apparent from the figure, the persistence of chlorpyrifos is increased significantly providing that degradation products especially chlorpyrifos oxon are regarded. TCP has a lower contribution to joint persistence as compared to parent product mainly because only 2 % of CP turns into TCP. On the other hand, chlorpyrifos oxon has a higher contribution to joint one due to its higher fraction of formation (89%). Hence, joint persistence exceeds the overall threshold that was proposed as 100 days by Webster and colleagues (1998).

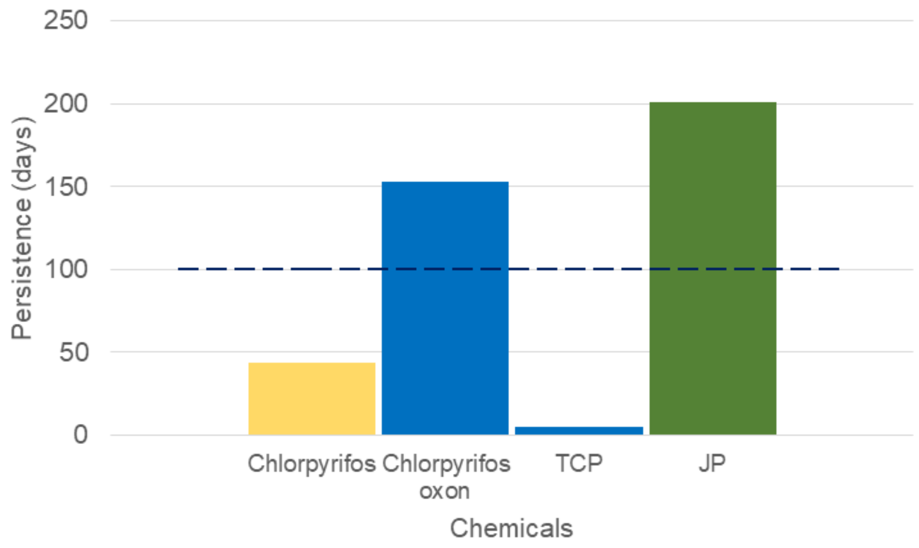


Figure 4.43. Persistence of chlorpyrifos family with a dashed line that is P_{ov} criterion of 100 days (Webster et al., 1998).

The predictive capability of EPI Suite and the effects of physicochemical inputs on chemical amount and persistence can be analyzed in Table 4.24. The percentage differences between EPI Suite predicted and final adjusted values for melting point, K_H and K_{oc} are two orders of magnitude, but these differences could not generate any effect on chemical amount and persistence.

This is mainly because the compound has low partitioning into the air when introduced into the soil (i.e. <1% as can be seen in Table 4.23). Even though differences between FAV and EPI Suite prediction for vapor pressure, solubility, K_{ow} are valid, these differences could not create any effect on persistence. Percent differences between final adjusted and EPI Suite predicted half-life in water and soil are three and four orders of magnitude, respectively. As a result, half-life in water only generates one order of magnitude in percent difference of persistence and chemical amount. However, half-life in soil generates two orders of magnitude. Overall, half-life in soil should be determined carefully as much as possible.

Table 4.24 Effect of FAV and EPI Suite predicted inputs on chlorpyrifos amount and persistence with percentage difference.

Chem	FAV	EPI Suite Value	Diff. Btw Inputs as %	Chem Amount (mole)	Persistence (d)	Percent Diff (%)
chlorpyrifos				2.96E+06	43	
chlorpyrifosmeltpred	4.20E+01	8.29E+01	-97	2.96E+06	43	0
chlorpyrifosvaporpred	1.72E-03	3.91E-03	-127	2.96E+06	43	0
chlorpyrifossolubpred	9.65E-01	7.68E+00	-696	2.96E+06	43	0
chlorpyrifosHenrypred	6.24E-01	1.79E-01	71	2.96E+06	43	0
chlorpyrifosairhalfpred	6.00E+00	3.00E+00	50	2.96E+06	43	0
chlorpyrifoswaterpred	5.76E+02	4.32E+03	-650	2.98E+06	43	1
chlorpyrifossoilpred	7.20E+02	8.64E+03	-1100	3.46E+07	506	91
chlorpyrifossedpred	5.76E+02	3.89E+04	-6653	2.96E+06	43	0
chlorpyrifoslogKowpred	4.91E+00	5.01E+00	-2	2.96E+06	43	0
chlorpyrifosKocpred	6.03E+03	7.28E+03	-21	2.96E+06	43	0
chlorpyrifospredicted				3.53E+07	516	92

The sensitivity analysis for the chlorpyrifos family is indicated in Figure 4.44. According to this figure, half-life in soil is the most sensitive parameter for all members of this family. This is consistent with the information presented in

Table 4.24. Furthermore, half-life in water and K_{oc} has a significant impact on CPO and TCP.

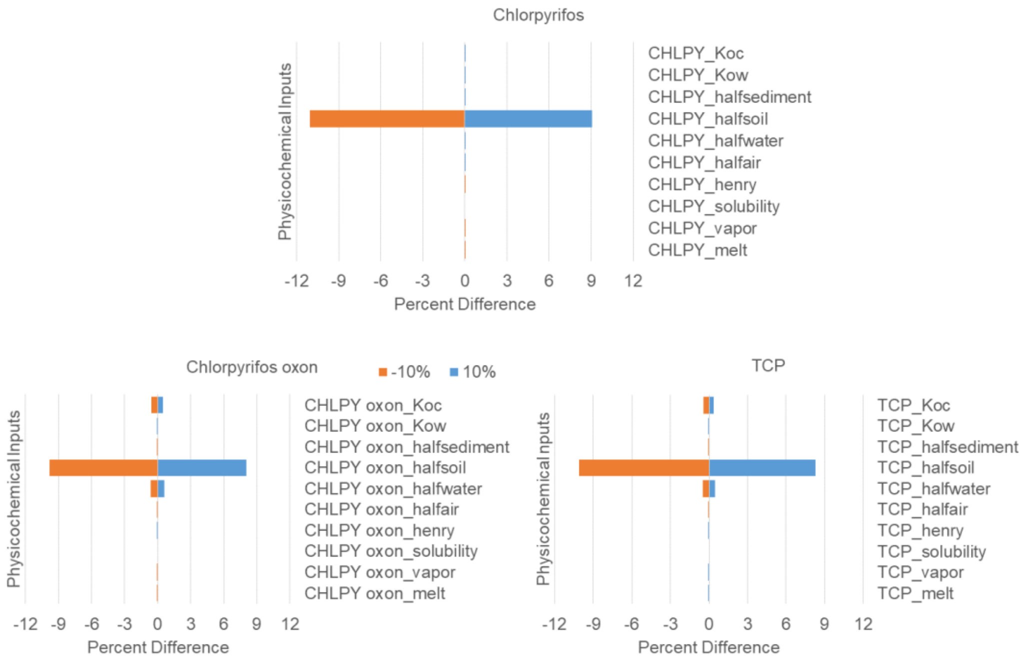


Figure 4.44. Sensitivity analysis result for chlorpyrifos and its TPs, namely, chlorpyrifos oxon, and TCP.

4.10 Chlorfenvinphos (CFVP)

Chlorfenvinphos (2-chloro-1-(2’, 4’-dichloro-phenyl) vinyl diethyl phosphate) is an organophosphorus insecticide. It could enter the environment by runoff or leaching from waste sites. Hence, it might be detected in soil, groundwater, or surface waters. It can damage the nervous system of humans and animals. Although chlorfenvinphos exposure at high dose kills humans, its chronic exposure effects on humans are unknown (ATSDR, 1997a).

4.10.1 Degradation Pathway Scheme for Chlorfenvinphos

A major amount of CFVP could accumulate in the soil medium, and major its TPs, namely desethyl-chlorfenvinphos, and (2’, 4’-dichlorophenyl) ethan-1, 2-diol can be detected in soil (Beynon, 1967). All TPs were determined in wet unsterilized soil samples four months after spiking soil with 15 ppm CFVP (Beynon, 1967). Therefore, the degradation mechanism might occur due to anaerobic biodegradation. Figure 4.45 shows the degradation scheme of chlorfenvinphos.

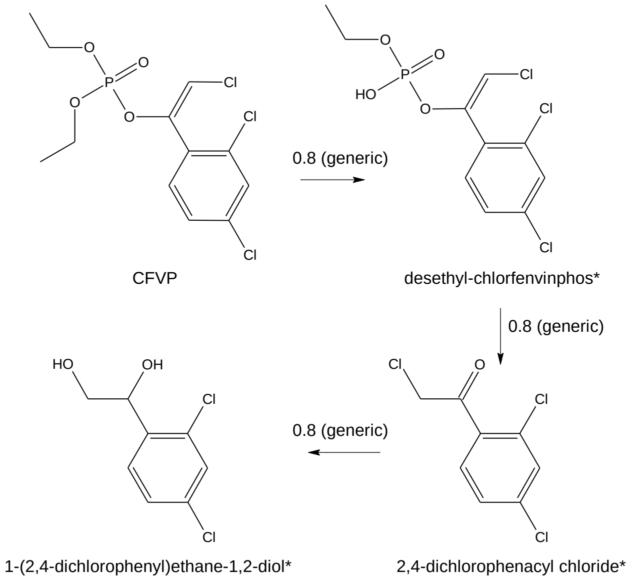


Figure 4.45. Degradation scheme of chlorfenvinphos (Beynon, 1967*). Number on each arrow indicates the fraction of formation.

4.10.2 Physicochemical Properties for Chlorfenvinphos Family

Compiled literature derived physicochemical property of parent chemical and EPI Suite predicted TPs are presented in Appendix A-Table A1. FAVs for parent chemical and its TPs are given in Appendix A- Table A2.

4.10.3 Evaluation and Persistency of Chlorfenvinphos Family

Table 4.25 indicates the environmental mass distribution of the substance family, total mass, and persistence. Soil and water are important media for this family. When the remaining compound mass in water medium is considered following its emission into soil medium, it can be said that soil/water run-off from soil to water is more probable for TPs when compared to the parent compound.

All members can accumulate as low amounts in sediment medium. While desethyl-CFVP could not accumulate in the air phase, low amounts of other members can be detected in air. When directly introduced into the air, the second degradation product, namely 2-4-dichlorophenacyl chloride accumulates appreciably in the air phase owing to its significantly higher vapor pressure and half-life in air. Persistence of CFVP is very low in the aqueous phase when compared to persistence in other media as well as its TPs. The main reason is the really low half-life (i.e. 1.28 hr) in water as obtained from (Mackay et al., 2006). All TPs have half-lives about three orders of magnitude higher.

Table 4.25. Amount of chlorfenvinphos & its TPs as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
Chlorfenvinphos	Air	1.75E+03	0	1.85E+02	0	3.57E+06	100	1.80E+01	0	3.57E+06	3569
	Water	9.45E-05	0	1.85E+03	91	1.92E-01	0	1.79E+02	9	2.03E+03	2
	Soil	8.62E-01	0	8.32E+01	0	5.56E+06	100	8.07E+00	0	5.56E+06	5555
	All three	5.85E+02	0	7.05E+02	0	3.04E+06	100	6.83E+01	0	3.04E+06	3042
Desethyl-chlorfenvinphos	Air	0.00E+00	0	1.33E+06	66	6.70E+05	34	2.60E+03	0	2.00E+06	2500
	Water	0.00E+00	0	1.66E+06	100	0.00E+00	0	3.25E+03	0	1.67E+06	2082
	Soil	0.00E+00	0	1.29E+06	63	7.45E+05	37	2.53E+03	0	2.04E+06	2546
	All three	0.00E+00	0	1.43E+06	75	4.72E+05	25	2.79E+03	0	1.90E+06	2376
2,4-dichlorophenacyl chloride	Air	1.27E+05	13	2.07E+05	22	6.07E+05	64	3.52E+03	0	9.44E+05	1476
	Water	4.66E+03	0	1.29E+06	96	2.22E+04	2	2.19E+04	2	1.34E+06	2086
	Soil	4.33E+03	0	1.75E+05	7	2.25E+06	93	2.98E+03	0	2.44E+06	3806
	All three	4.55E+04	3	5.56E+05	35	9.61E+05	61	9.46E+03	1	1.57E+06	2456
1-(2,4-dichlorophenyl) ethane-1,2-diol	Air	2.95E+02	0	3.84E+05	42	5.34E+05	58	9.28E+02	0	9.19E+05	1794
	Water	5.59E-03	0	6.65E+05	100	1.01E+01	0	1.61E+03	0	6.66E+05	1302
	Soil	9.10E-01	0	3.62E+05	37	6.06E+05	63	8.75E+02	0	9.69E+05	1892
	All three	9.88E+01	0	4.70E+05	55	3.80E+05	45	1.14E+03	0	8.51E+05	1663

By using Table 4.25, the environmental mass of compounds in various environmental compartments was plotted regarding several emission scenarios in Figure 4.46. CFVP emission into only soil, desethyl-CFVP emission into only water seems to be affected by mode-of-entry. 2,4-dichlorophenacylchloride and 1-(2,4-dichlorophenyl)ethane-1,2-diol emission into only soil and only water cause the highest chemical amounts in the relevant medium.

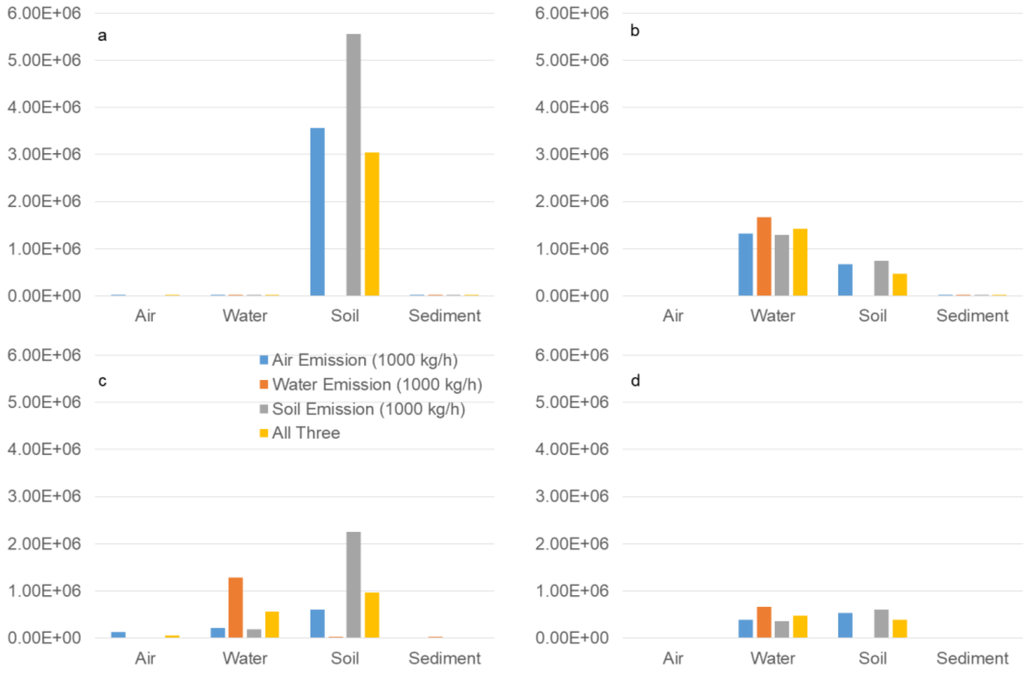


Figure 4.46. Amount (kg) of (a) CFVP, (b) desethyl-CFVP, (c) 2,4-dichlorophenacylchloride, and (d) 1-(2,4-dichlorophenyl)ethane-1,2-diol.

The individual persistence of chlorfenvinphos and its TPs, together with their joint persistence is demonstrated in Figure 4.47. From the figure, the persistence of CFVP is more than doubled when TPs are considered.

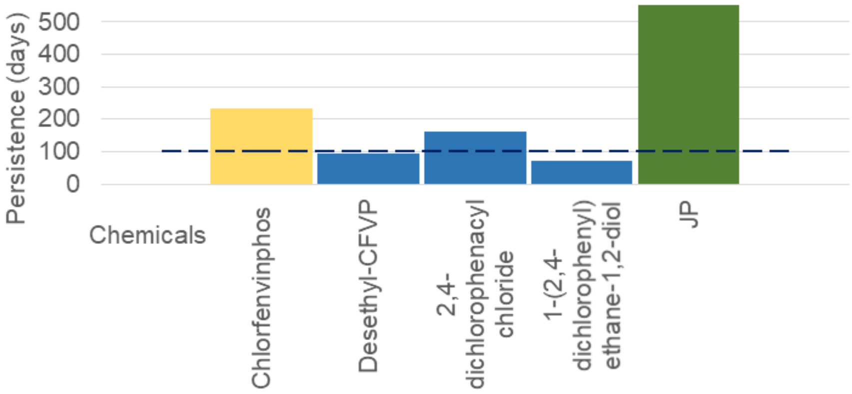


Figure 4.47. Persistence of CFVP family with a dashed line that is overall persistence criterion (P_{ov}) of 100 days (Webster et al., 1998)

The predictive capability of EPI Suite and the effects of physicochemical inputs on chemical amount and persistence can be analyzed in Table 4.26. Although differences between FAV and EPI Suite prediction for melting point, vapor pressure, solubility, and partition coefficient are valid, these differences could not create any effect on chemical amount and persistence. FAV and EPI Suite predicted half-life in water and soil are different from each other six and two orders of magnitude in percentage, respectively. For this reason, the percent differences in chemical amount and persistence are one and two orders of magnitude, respectively. Such a great difference in water half-life causes a relatively small change in persistence because CFVP partition only slightly in water. Overall, half-life in soil should be determined carefully. Additionally, half-life in water determination has secondary importance with respect to persistence and chemical amount distribution.

Table 4.26. Effect of FAV and EPI Suite predicted inputs on CFVP amount and persistence with percentage difference.

Chem	**FAV**	**EPI Suite Value**	**Diff. Btw Inputs as %**	**Chem Amount (mole)**	**Persistence (d)**	**Percent Diff (%)**
CFVP				1.54E+07	231	
CFVPmeltpred	-1.90E+01	8.59E+01	552	1.55E+07	231	0
CFVPvaporpred	1.00E-04	7.70E-04	-670	1.55E+07	231	0
CFVPsolubpred	1.24E+02	3.24E+01	74	1.54E+07	231	0
CFVPHenrypred	2.90E-04	8.56E-03	-2852	1.54E+07	230	0
CFVPwaterpred	1.00E+00	1.44E+03	-143900	1.57E+07	236	2
CFVPsoilpred	4.03E+03	2.88E+03	29	1.12E+07	168	-38
CFVPlogKowpred	3.52E+00	4.16E+00	-18	1.54E+07	231	0
CFVPKocpred	1.29E+03	1.26E+03	2	1.54E+07	231	0
CFVPpredicted				1.13E+07	170	-36

Sensitivity analysis for chlorfenvinphos family is shown in Figure 4.48. According to this figure, a ten percent decrease in vapor pressure of chlorfenvinphos generate a remarkable decrease (around 450%) in persistence. This enormous change in persistence observed during sensitivity analysis is not consistent with the results reported in Table 4.26. As can be seen from the table, -670% difference in vapor pressure of CFVP did not result in any change in persistence. This response of the EQC model could not be understood. For desethyl-CFVP, half-life in water and soil are sensitive parameters in decreasing order. Half-life in soil, water, and K_{oc} are ordered in decreasing importance for 2, 4-dichlorophenacyl chloride and 1-(2, 4-dichlorophenyl) ethane-1, 2-diol.

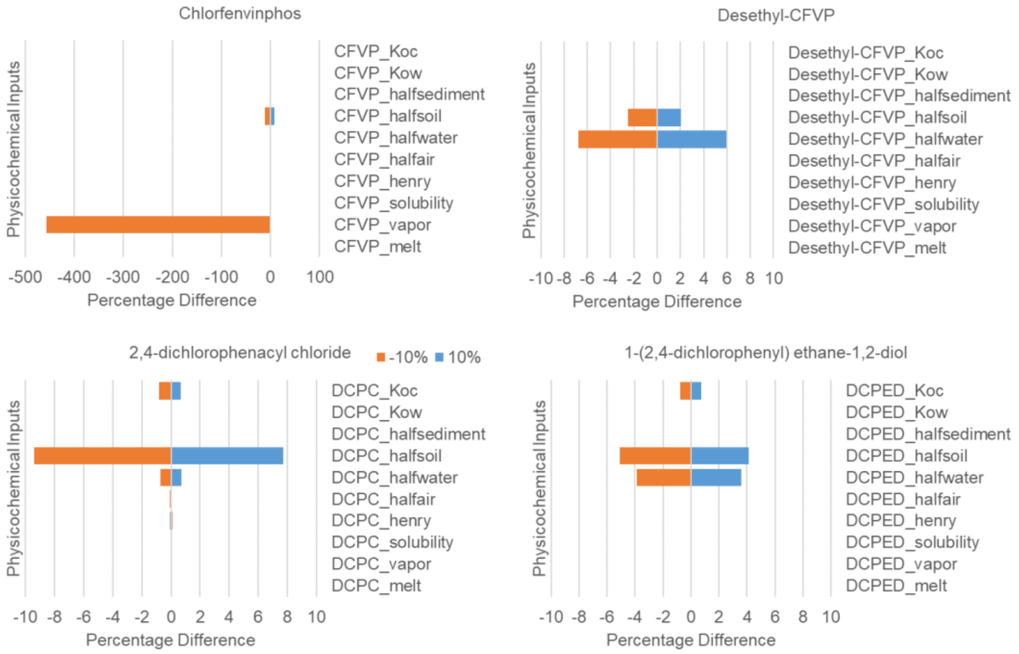


Figure 4.48. Sensitivity analysis result for chlorfenvinphos and its TPs, namely, desethyl-CFVP, 2, 4-dichlorophenacyl chloride, and 1-(2, 4-dichlorophenyl) ethane-1, 2-diol.

4.11 Pentachlorobenzene (PeCB)

Pentachlorobenzene was used as a fungicide and a flame retardant. However, it is not being used anymore (Denier van der Gon et al., 2007). It could not be classified as a human carcinogen due to a lack of valid studies (UNEP, 2017). On the other hand, it is very toxic to the aquatic ecosystem (“Pentachlorobenzene”, 2020). Moreover, it is very persistent under natural conditions (Jayachandran et al., 2003).

4.11.1 Degradation Pathway Scheme for Pentachlorobenzene

Reductive dechlorination is possible for chlorinated benzene congeners in contaminated sediment (Pavlostathis & Prytula, 2000). For reductive dechlorination, microorganisms are necessary. Dominant congeners for TPs are 1,2,3,5-

tetrachlorobenzene, 1,3,5-trichlorobenzene, and 1,3-dichlorobenzene. On the other hand, 1,2,4,5-tetrachlorobenzene and 1,2,4-trichlorobenzene can form in low concentrations (Pavlostathis & Prytula, 2000). While monobenzene is observed as an only end product in the laboratory studies, 1,3,5-TCB, and 1,3-DCB are observed end products in the environment (Beurskens et al., 1994). Additionally, the dechlorination rate is slower in the field studies compared to laboratory studies (Beurskens et al., 1994). Figure 4.49 indicates the degradation scheme of pentachlorobenzene.

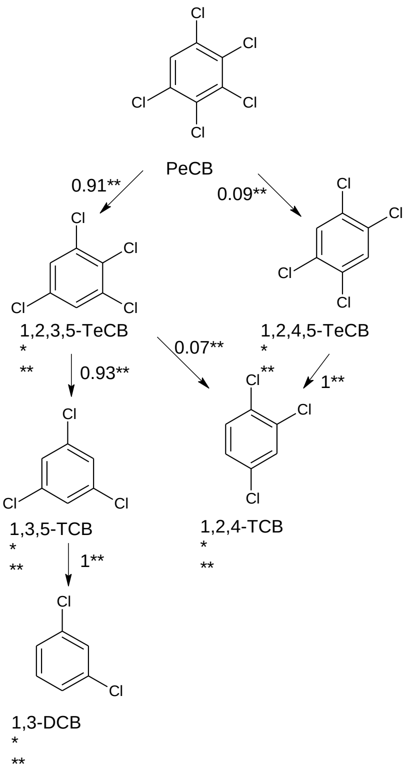


Figure 4.49. Degradation scheme of pentachlorobenzene (Beurskens et al., 1994*; Pavlostathis & Prytula, 2000**). Number on each arrow indicates fraction of formation of TPs.

4.11.2 Physicochemical Properties for Pentachlorobenzene Family

Compiled literature derived physicochemical property and EPI Suite estimated ones for parent chemical and TPs are presented in Appendix A-Table A1. FAVs for parent chemical and its TPs are given in Appendix A- Table A2.

4.11.3 Evaluation and Persistency of Pentachlorobenzene Family

Table 4.27 demonstrates the environmental mass distribution of the substance family, total mass, and persistence. It is apparent from the table that the PeCB family has a much larger presence in air medium when compared to the other studied chemicals. Except for introduction into the soil, all other modes of entry results in greater than 15% of the mass accumulating in the air. This is partly due to high vapor pressure, but also due to lack of degradation mechanisms for PeCB and its TPs in air.

Table 4.27. Amount of pentachlorobenzene & its TPs as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
PeCB	Air	4.68E+06	74	2.23E+05	4	1.40E+06	22	5.04E+03	0	6.31E+06	6307
	Water	3.31E+06	68	5.73E+05	12	9.90E+05	20	1.29E+04	0	4.89E+06	4890
	Soil	1.09E+05	1	6.34E+03	0	1.22E+07	99	1.43E+02	0	1.23E+07	12315
	All three	2.70E+06	34	2.67E+05	3	4.86E+06	62	6.04E+03	0	7.84E+06	7838
1,2,3,5-TeCB	Air	1.59E+06	81	4.20E+04	2	1.30E+05	7	1.91E+05	10	1.96E+06	2148
	Water	1.17E+06	35	3.66E+05	11	9.57E+04	3	1.67E+06	51	3.30E+06	3622
	Soil	3.48E+04	1	1.35E+03	0	3.70E+06	99	6.14E+03	0	3.74E+06	4113
	All three	9.31E+05	31	1.36E+05	5	1.31E+06	44	6.22E+05	21	3.00E+06	3295
1,2,4,5-TeCB	Air	3.14E+05	71	1.75E+04	4	3.16E+04	7	7.99E+04	18	4.43E+05	4920
	Water	2.20E+05	43	4.94E+04	10	2.21E+04	4	2.25E+05	44	5.17E+05	5744
	Soil	3.33E+03	1	2.34E+02	0	3.70E+05	99	1.07E+03	0	3.75E+05	4165
	All three	1.79E+05	40	2.24E+04	5	1.41E+05	32	1.02E+05	23	4.45E+05	4943
1,3,5-TCB	Air	4.53E+05	85	1.10E+04	2	3.55E+04	7	3.07E+04	6	5.30E+05	627
	Water	3.48E+05	22	3.21E+05	20	2.72E+04	2	8.93E+05	56	1.59E+06	1878
	Soil	1.78E+04	1	1.00E+03	0	3.38E+06	99	2.79E+03	0	3.40E+06	4018
	All three	2.73E+05	15	1.11E+05	6	1.15E+06	62	3.09E+05	17	1.84E+06	2174
1,2,4-TCB	Air	1.01E+05	87	2.00E+03	2	7.74E+03	7	5.69E+03	5	1.17E+05	761
	Water	7.82E+04	26	5.71E+04	19	5.97E+03	2	1.62E+05	53	3.04E+05	1976
	Soil	4.76E+03	1	1.93E+02	0	6.09E+05	99	5.48E+02	0	6.14E+05	3997
	All three	6.15E+04	18	1.98E+04	6	2.08E+05	60	5.62E+04	16	3.45E+05	2245
1,3-DCB	Air	4.30E+05	94	4.82E+03	1	1.77E+04	4	2.69E+03	1	4.56E+05	538
	Water	3.17E+05	42	2.75E+05	36	1.31E+04	2	1.54E+05	20	7.59E+05	897
	Soil	6.51E+04	3	1.55E+03	0	1.87E+06	97	8.62E+02	0	1.93E+06	2286
	All three	2.71E+05	26	9.39E+04	9	6.33E+05	60	5.24E+04	5	1.05E+06	1240

According to Table 4.27, the environmental mass of compounds was plotted concerning several media under different emission scenarios in Figure 4.50. Mode-of-entry of pentachlorobenzene to only air, only soil, and mode-of-entry of other compounds to only soil medium or to only air medium cause higher mass of the compound in the emitted medium.

Figure 4.50. Amount (kg) of (a) pentachlorobenzene, (b) 1, 2, 4, 5-TeCB, (c) 1, 2, 3, 5-TeCB, (d) 1, 2, 4-TCB, (e) 1, 3, 5-TCB and (f) 1, 3-DCB.

The individual persistence of pentachlorobenzene and its TPs, together with their joint persistence are indicated in Figure 4.51. As is apparent from this figure, none of the TPs exceed the persistence of PeCB, yet the main TPs of PeCB, i.e. 1, 2, 3, 5 TeCB, 1, 3, 5-TCB, 1, 3-DCB have a persistence that still exceeds the proposed (Webster et al., 1998) level of 100 days. Overall, the persistence of pentachlorobenzene is increased noticeably when TPs are included. Joint persistence exceeds threshold value excessively.

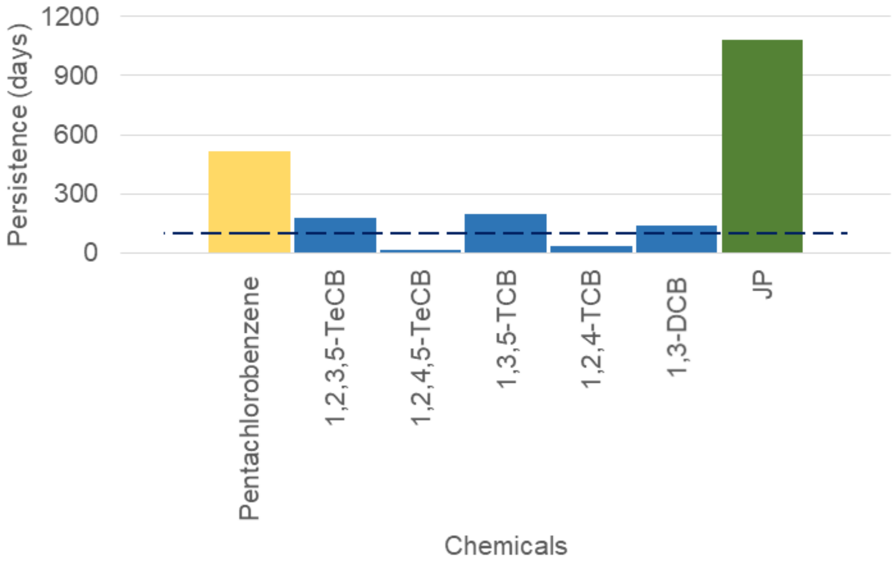


Figure 4.51. Persistence of pentachlorobenzene family with a dashed line that is P_{ov} criterion of 100 days (Webster et al., 1998).

The predictive capability of EPI Suite and the effects of physicochemical inputs on chemical amount and persistence can be analyzed in Table 4.28. The percentage differences between EPI Suite predicted and FAVs for melting point, vapor pressure, solubility, and K_{oc} are two orders of magnitude. Only underpredicted K_{oc} generate a decrease in persistence, other aforementioned inputs do not have an effect on persistence. Furthermore, the percentage difference between FAV and EPI Suite predicted half-life in sediment is six orders of magnitude. It only results in a 1% increase in persistence and chemical amount. The main reason for this is, can be seen from Table 4.27, PeCB does not partition much into sediments. Hence, any change in sediment half-life does not affect persistence significantly. Rather than half-life in sediment, K_{oc} is an influential parameter.

The sensitivity analysis for pentachlorobenzene family is represented in Figure 4.52. From this figure, half-life in soil is the most sensitive parameter for all members. Furthermore, K_{oc} and K_H become important for 1, 3, 5-TCB, 1, 2, 4-TCB, and 1, 3-DCB.

Table 4.28. Effect of FAV and EPI Suite predicted inputs on pentachlorobenzene amount and persistence with percentage difference.

Chem	FAV	EPI Suite Value	Diff. Btw Inputs as %	Chem Amount (mole)	Persistence (d)	Percent Diff (%)
PeCB				4.92E+07	513	
PeCBmeltpred	8.60E+01	6.45E+01	25	4.92E+07	513	0
PeCBvaporpred	2.19E-01	3.34E-01	-53	4.92E+07	513	0
PeCBsolubpred	6.56E-01	1.01E+00	-54	4.92E+07	513	0
PeCBHenrypred	8.37E+01	8.28E+01	1	4.92E+07	513	0
PeCBsedpred	2.90E+01	3.89E+04	-134038	4.97E+07	518	1
PeCBlogKowpred	5.18E+00	5.21E+00	-1	4.92E+07	513	0
PeCBKocpred	8.13E+04	3.71E+03	95	4.22E+07	440	-17
PeCBpredicted				4.26E+07	444	-16

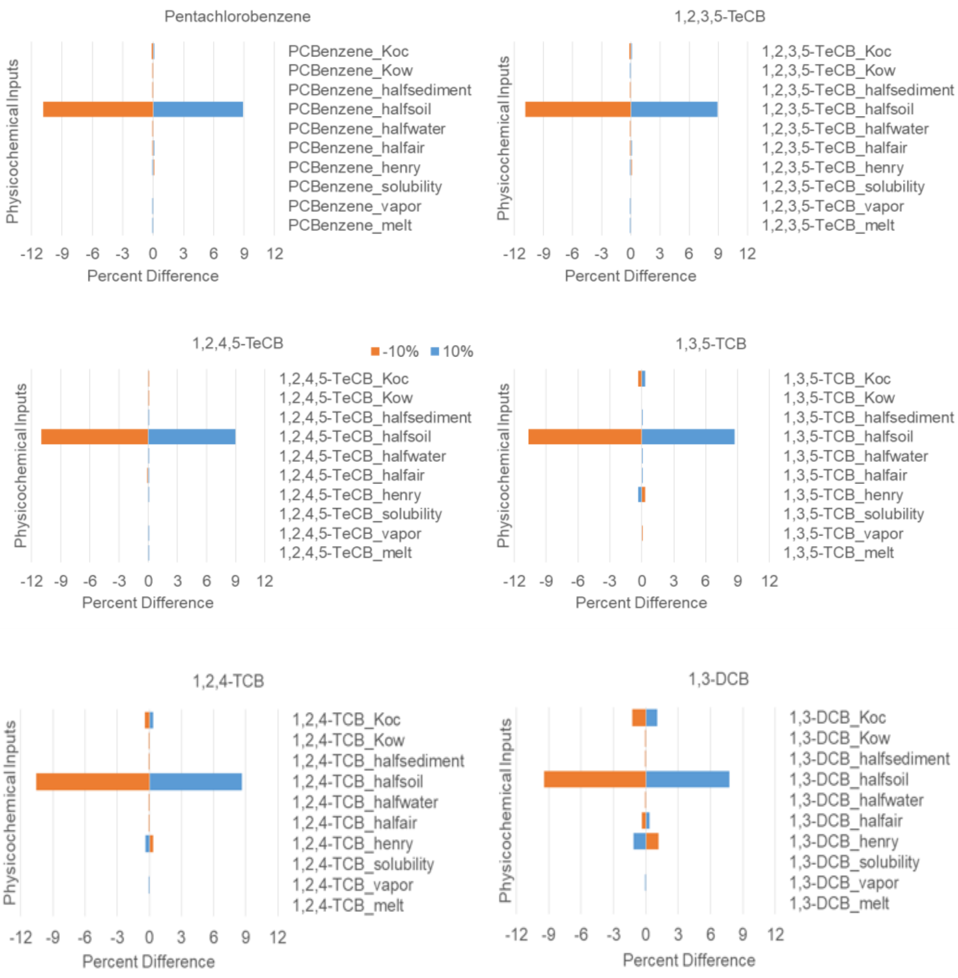


Figure 4.52. Sensitivity analysis result for pentachlorobenzene and its TPs, namely, 1, 2, 3, 5-TeCB, 1, 2, 4, 5-TeCB, 1, 3, 5-TCB, 1, 2, 4-TCB, and 1, 3-DCB.

4.12 Trichloromethane

Trichloromethane or chloroform is used in chemical and paper industries. It evaporates rapidly in case of contact with air. It also dissolves easily in water, but it does not tend to bind to soil. Although it is unknown that chloroform cause birth defects, reproductive effects, and cancerogenic effect on humans, animal studies show that abnormalities, miscarriages, and cancer were observed in rats, and mice (ATSDR, 1997b).

4.12.1 Degradation Pathway Scheme for Trichloromethane

Nanoscale metal particles can transform trichloromethane that is one of the common pollutants in soils and aquifers. The dominant product is methane with a fraction of the formation of 0.7, but the only chlorinated TP is dichloromethane (DCM). Methane formation from DCM is slower as compared to methane formation from trichloromethane (Lien & Zhang, 1999). Therefore, methane formation from DCM was not considered in this study. A catalyst such as palladium or palladium with alumina can be added to metal particles to speed up hydrodehalogenation (Lien & Zhang, 1999; Lowry & Reinhard, 1999).

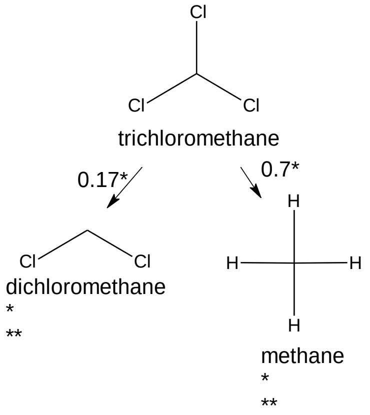


Figure 4.53. Degradation scheme of trichloromethane (Lien & Zhang, 1999*; Lowry & Reinhard, 1999**). Number on each arrow indicates the fraction of formation of TPs from the parent compound.

4.12.2 Physicochemical Properties for Trichloromethane Family

Compiled literature derived physicochemical property for parent chemical, literature derived and EPI Suite estimated ones for TPs are presented in Appendix A-Table A1. FAVs for parent chemical and its TPs are given in Appendix A- Table A2.

4.12.3 Evaluation and Persistency of Trichloromethane Family

Table 4.29 shows the environmental mass distribution of the substance family, total mass, and persistence. Air is the main medium for all members regardless of the emission scenario. Intermedia transport processes between air and soil/water are considerable mechanisms for all members. High amounts in air medium could indicate high mobility of this family and their long-range transport probability. Also, low amounts of trichloromethane, dichloromethane, and methane can be found in soil and sediment media.

Table 4.29. Amount of trichloromethane & its TPs as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
Trichloromethane	Air	2.43E+06	99	2.52E+04	1	2.72E+03	0	8.63E+01	0	2.46E+06	2455
	Water	2.07E+06	84	3.83E+05	16	2.32E+03	0	1.31E+03	0	2.46E+06	2456
	Soil	2.40E+06	96	3.03E+04	1	6.32E+04	3	1.04E+02	0	2.50E+06	2497
	All three	2.30E+06	93	1.46E+05	6	2.27E+04	1	5.00E+02	0	2.47E+06	2469
Dichloromethane	Air	4.11E+05	99	5.44E+03	1	3.26E+02	0	1.34E+01	0	4.17E+05	2455
	Water	3.50E+05	84	6.69E+04	16	2.78E+02	0	1.65E+02	0	4.17E+05	2455
	Soil	4.08E+05	97	6.57E+03	2	7.54E+03	2	1.62E+01	0	4.22E+05	2484
	All three	3.90E+05	93	2.63E+04	6	2.71E+03	1	6.48E+01	0	4.19E+05	2464
Methane	Air	3.44E+07	100	1.66E+02	0	1.25E+03	0	3.32E-01	0	3.44E+07	49102
	Water	1.94E+07	99	1.58E+05	1	7.03E+02	0	3.16E+02	0	1.96E+07	27964
	Soil	3.43E+07	100	1.67E+02	0	2.66E+03	0	3.34E-01	0	3.43E+07	49008
	All three	2.94E+07	100	5.29E+04	0	1.54E+03	0	1.06E+02	0	2.94E+07	42025

Based on Table 4.29, the environmental mass of compounds was plotted regarding several media under different emission scenarios in Figure 4.54. Mode-of entry effect can be recognized for all members in case of emission into only air medium. No matter which media the compound family is introduced to, only presence in air media is notable.

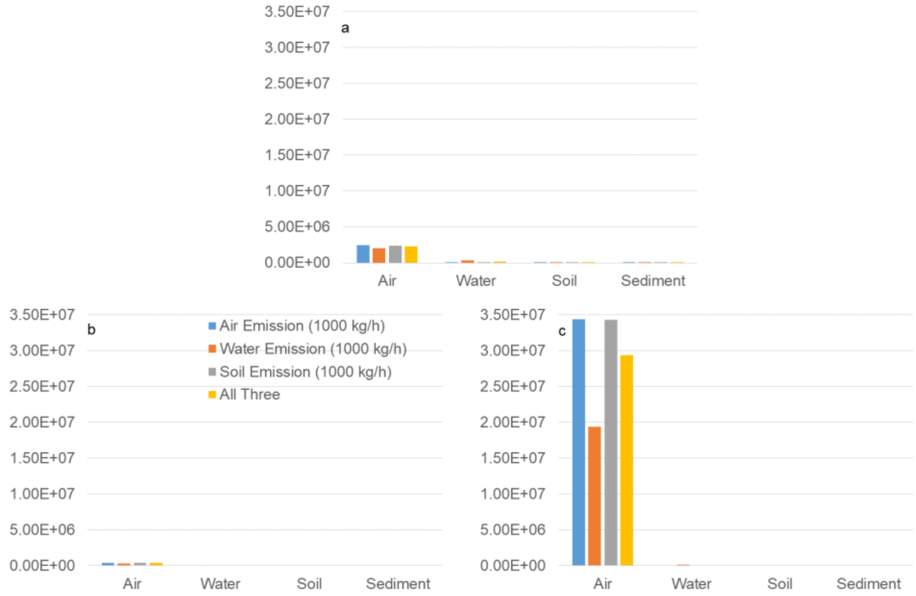


Figure 4.54. Amount (kg) of (a) trichloromethane, (b) DCM, and (c) methane in the environment.

The individual persistence of trichloromethane and its TPs, together with their joint persistence are presented in Figure 4.55. Here persistences are calculated for air medium as the mode-of-entry. This is different from the other compounds reported so far. Air was selected as the mode-of-entry for trichloromethane because of its dominance in this medium and that it would be the most probable form of an entry in the environment. From Figure 4.55, the persistence of trichloromethane and dichloromethane are 102 and 24 days, respectively. However, the significantly higher persistence of methane dominates the whole family.

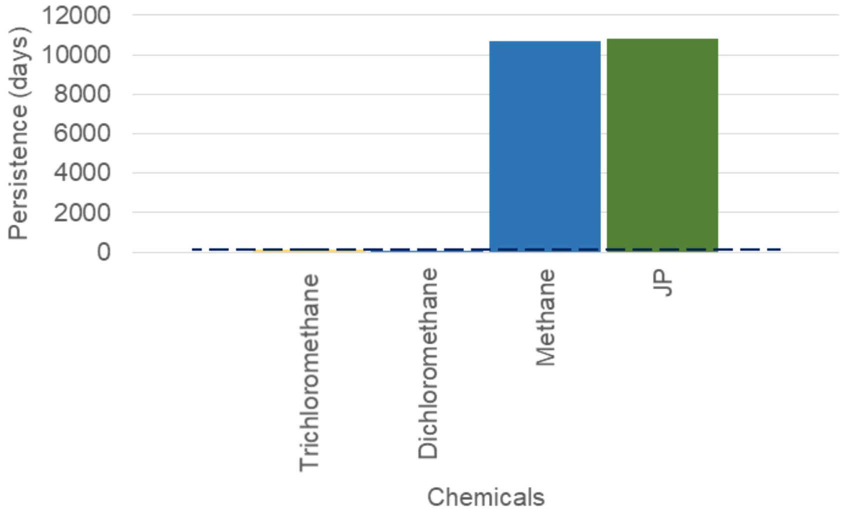


Figure 4.55. Persistence of trichloromethane family with a dashed line that is P_{ov} criterion of 100 days (Webster et al., 1998).

The predictive capability of EPI Suite and the effects of physicochemical inputs on chemical amount and persistence can be analyzed in Table 4.30. The percentage differences between EPI Suite predicted and FAV for melting point, vapor pressure, solubility, $K_{H,}$ $\log K_{ow}$ and K_{oc} are present. However, any of the aforementioned physicochemical properties do not generate any difference in chemical amount and persistence. On the other hand, a deviation in half-life in air and water generate a 30% and -1% change in chemical amount and persistence. Since air is the dominant medium for trichloromethane, any impact on air half-life would be expected to have an impact on persistence.

Table 4.30. Effect of FAV and EPI Suite predicted inputs on trichloromethane amount and persistence with percentage difference.

Chem	FAV	EPI Suite Value	Diff. Btw Inputs as %	Chem Amount (mole)	Persistence (d)	Percent Diff (%)
TCM				2.06E+07	102	
TCMmeltpred	-6.34E+01	-7.89E+01	-24	2.06E+07	102	0
TCMvaporpred	2.72E+04	2.46E+04	10	2.06E+07	102	0
TCMsolubpred	7.90E+03	8.81E+03	-12	2.06E+07	102	0
TCMHenrypred	4.11E+02	3.33E+02	19	2.06E+07	102	0
TCMairhalfpred	1.70E+03	2.45E+03	-44	2.95E+07	147	30
TCMwaterpred	1.70E+03	9.00E+02	47	2.04E+07	101	-1
TCMsoilpred	5.50E+03	1.80E+03	67	2.06E+07	102	0
TCMsedpred	1.70E+04	8.10E+03	52	2.06E+07	102	0
TCMlogKowpred	2.03E+00	1.69E+00	17	2.06E+07	102	0
TCMKocpred	2.88E+01	3.18E+01	-10	2.06E+07	102	0
TCMpredicted				2.90E+07	144	29

The sensitivity analysis for the trichloromethane family is shown in Figure 4.56. According to this figure, half-life in the air is the most sensitive parameter for all members of this family. These results are consistent with the above discussion regarding Table 4.30.

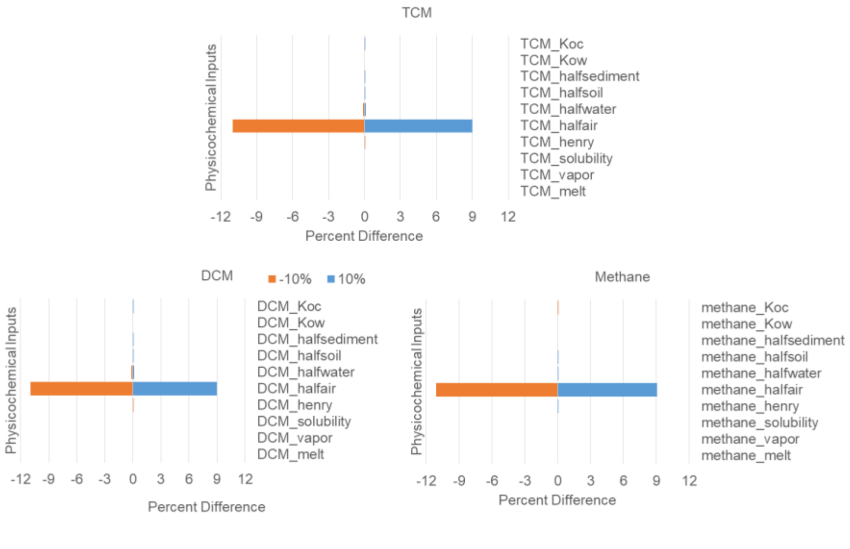


Figure 4.56. Sensitivity analysis result for trichloromethane and its TPs, namely, DCM, and methane.

4.13 Aclonifen (AFN)

Aclonifen (2-chloro-6-nitro-3-phenoxyaniline) is one of the nitrophenyl ether herbicides. This herbicide is used for pre-emergence control of weed and grass species in sunflower fields. It has very low acute toxicity and it is not skin or eye irritant, but it has skin sensitizing property. It might be evaluated as moderate or highly persistent in the soil since it is not readily biodegradable (EFSA, 2008).

4.13.1 Degradation Pathway Scheme for Aclonifen

Aclonifen degradation was studied using thermo-sensitive hybrid microgels (Mutharani et al., 2020). Conductive polymers could be modified with inorganic metal nanoparticles. Then, microgels can be added to this combination, so hybrid microgels can be obtained.

–NO_2 group in aclonifen can be reduced to –NHOH group via the aid of the transfer process of four electrons and four protons. This electrochemical reduction causes a transformation from aclonifen to its TP, namely 3-chloro-N1-hydroxy-4-phenoxybenzene-1, 2-diamine (Mutharani et al., 2020). This reaction mechanism may not take place under environmental conditions, nevertheless, it was one of the two studies that could be found in the literature on degradation products of aclonifen. The degradation scheme of aclonifen is represented in Figure 4.57.

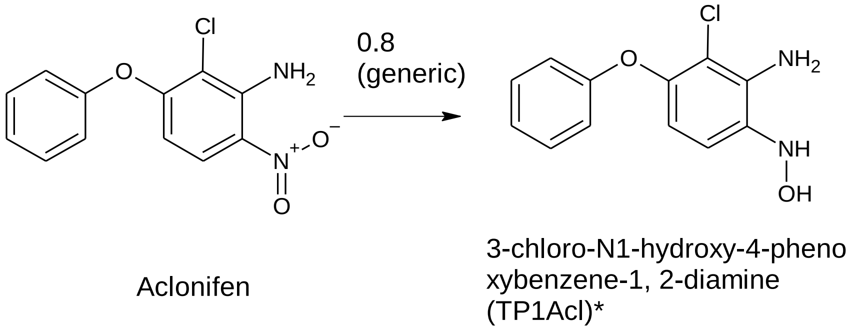


Figure 4.57. Degradation scheme of aclonifen (Mutharani et al., 2020*). Number on arrow indicates fraction of formation of TP from the parent compound.

4.13.2 Physicochemical Properties for Aclonifen Family

Compiled literature derived physicochemical property for parent chemical, EPI Suite estimated ones for parent compound, and TP are presented in Appendix A-Table A1. FAVs for parent chemical and its TP are given in Appendix A- Table A2.

4.13.3 Evaluation and Persistency of Aclonifen Family

Table 4.31 indicates the environmental mass distribution of the substance family, total mass, and persistence. Aclonifen tends to accumulate soil medium excluding aclonifen emission into water medium. A low amount of aclonifen can be found in water, air, and sediment media. In addition, deposition from air to soil could be a significant intermedia transport mechanism. Contrary to aclonifen, the main sink environmental compartment for its TP1Acl that is 3-chloro-N1-hydroxy-4-phenoxybenzene-1, 2-diamine is water. While low aclonifen amount can be detected in air, its transformation product does not distribute into the air. This is mainly due to much lower VP and extremely low K_{aw} (on the order of 10^{-13}) of TP1Acl when compared to aclonifen.

Table 4.31. Amount of aclonifen & its TP as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
Aclonifen	Air	7.76E+03	0	1.23E+04	0	2.63E+06	99	1.38E+02	0	2.65E+06	2649
	Water	1.46E-01	0	1.45E+05	99	4.94E+01	0	1.62E+03	1	1.47E+05	147
	Soil	5.40E+00	0	2.51E+03	0	3.98E+06	100	2.80E+01	0	3.98E+06	3984
	All three	2.59E+03	0	5.33E+04	2	2.20E+06	98	5.95E+02	0	2.26E+06	2260
TP1Acl	Air	0.00E+00	0	7.43E+05	56	5.91E+05	44	1.44E+03	0	1.34E+06	1670
	Water	0.00E+00	0	1.04E+06	100	0.00E+00	0	2.01E+03	0	1.04E+06	1301
	Soil	0.00E+00	0	7.10E+05	52	6.57E+05	48	1.37E+03	0	1.37E+06	1711
	All three	0.00E+00	0	8.31E+05	67	4.16E+05	33	1.61E+03	0	1.25E+06	1560

Based on Table 4.31, the environmental mass of aclonifen and TP1Acl was plotted considering various media under several emission scenarios in Figure 4.58. For aclonifen, mode-of-entry to only soil and only water causes a higher chemical amount in the emitted compartment. Additionally, the highest amount of TP1Acl in water can be explained by TP1Acl emission into the water medium, followed by very limited and slow intermedia transfer to sediment.

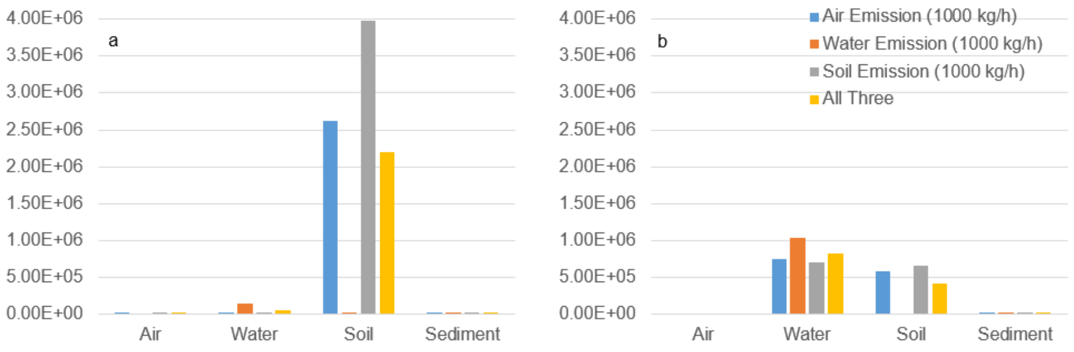


Figure 4.58. Amount (kg) of (a) aclonifen, and (b) TP1Acl in the environment.

Individual persistence of aclonifen and its TP, together with their joint persistence are demonstrated in Figure 4.59. From the figure, TP is not as persistent as aclonifen. Hence, aclonifen is the main contributor to joint persistence. TP1Acl may not necessarily be produced under environmental conditions, so when more information about potential degradation products of aclonifen is available, joint persistence can be re-evaluated.

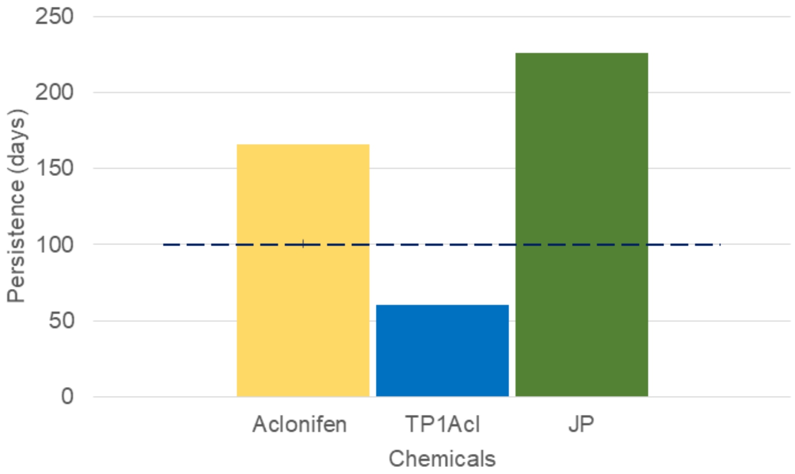


Figure 4.59. Persistence of aclonifen family with a dashed line that is P_{ov} criterion of 100 days (Webster et al., 1998).

The predictive capability of EPI Suite and the effects of physicochemical inputs on chemical amount and persistence can be analyzed in Table 4.32. The percentage differences between EPI Suite predicted and FAV for many physicochemical parameters do not have any effect on the chemical amount and persistence.

However, the percentage difference between two various vapor pressure inputs causes a significant change in chemical amount and persistence. When vapor pressure is increased to EPI Suite predicted value, a larger percentage of aclonifen partition into the water phase, which results in a higher degradation rate, lowering persistence. The half-life of aclonifen in water is 101 hours when compared to that in the soil of 2808 hours. This shorter half-life results in decreased persistence.

It should be noted that Table 4.32 does not include solubility because experimental solubility information could not be found for aclonifen, hence EPI predicted value was used in the EQC model. It is interesting however to note that in the sensitivity study explained below, vapor pressure has a much larger impact on persistence when compared to solubility. This is most probably related to the internal fugacity calculations of the EQC, as discussed in the final section of this chapter.

Table 4.32. Effect of FAV and EPI Suite predicted inputs on aclonifen amount and persistence with percentage difference.

Chem	FAV	EPI Suite Value	Diff. Btw Inputs as %	Chem Amount (mole)	Persistence (d)	Percent Diff (%)
AFN				1.51E+07	166	
AFNmeltpred	8.15E+01	1.60E+02	-96	1.51E+07	166	0
AFNvaporpred	2.11E-05	8.54E-05	-305	3.92E+06	43	-284
AFNHenrypred	1.29E-03	1.03E-03	20	1.51E+07	166	0
AFNwaterpred	1.01E+02	1.44E+03	-1326	1.52E+07	167	1
AFNsoilpred	2.81E+03	2.88E+03	-3	1.54E+07	170	2
AFNsedpred	3.43E+02	1.30E+04	-3690	1.51E+07	166	0
AFNlogKowpred	4.08E+00	3.71E+00	9	1.51E+07	166	0
AFNpredicted				9.62E+06	106	-56

Sensitivity analysis for aclonifen and its TP is represented in Figure 4.60. Ten percent decrease in vapor pressure of aclonifen causes a dramatic change in persistence, as was previously reported as an unexpected outcome for other compounds.

Excluding this case, half-life in soil could be a sensitive candidate if a ten percent decrease and increase are considered together. For TP1Acl, half-life in water and soil are sensitive parameters in decreasing order.

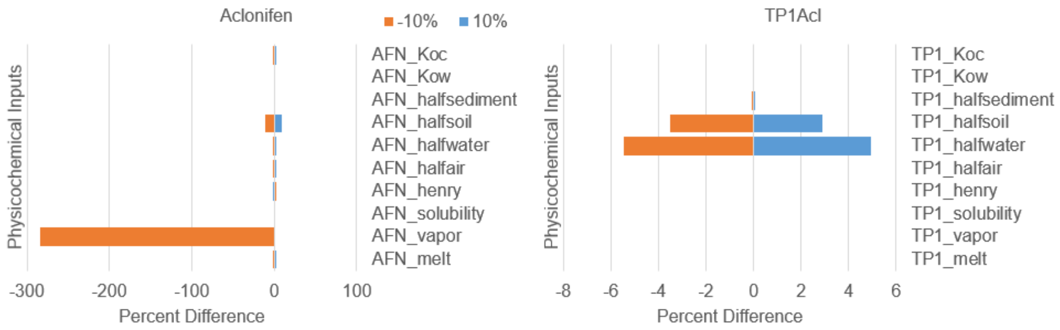


Figure 4.60. Sensitivity analysis result for aclonifen and TP1Acl, namely 3-chloro-N1-hydroxy-4-phenoxybenzene-1, 2-diamine.

4.14 Bifenox

Bifenox (methyl-5-(2,4-dichlorophenoxy-2-nitrobenzoate) is a nitrodiphenyl ether herbicide that could be combined with other herbicides to promote performance (Roy et al., 2004). It is effective for controlling broadleaf and grass weeds (Roger, 1975). It has low mammalian toxicity along with unidentified health problems, but it is moderately or highly toxic to aquatic organisms (Hertfordshire, 2020). It does not tend to leach to groundwater due to low solubility (Hertfordshire, 2020).

4.14.1 Degradation Pathway Scheme for Bifenox

Bifenox in aqueous isopropanol could be phototransformed under UV and sunlight in the presence of TiO_2 (Roy et al., 2004). In that study, transformation product methyl (2,4-dichlorophenoxy) anthranilate was detected in UV and sunlight initiated phototransformation. Reduction, dechlorination, nucleophilic displacement, and hydrolysis mechanisms were identified during phototransformation.

Methyl (2,4-dichlorophenoxy) anthranilate that is the dominant product results from the reduction of the nitro group in bifenox. The reduction of amino diphenyl ether contributes to successive hydrogen abstraction, so nitroso and hydroxyl amino compounds generate from bifenox (Roy et al., 2004). The degradation scheme of bifenox is represented in Figure 4.61. This TP was observed under laboratory photochemical degradation studies, therefore it is uncertain whether this compound would actually occur in the environment. Nevertheless, since there were no other TPs reported for bifenox, methyl (2,4-dichlorophenoxy) anthranilate was selected for this study.

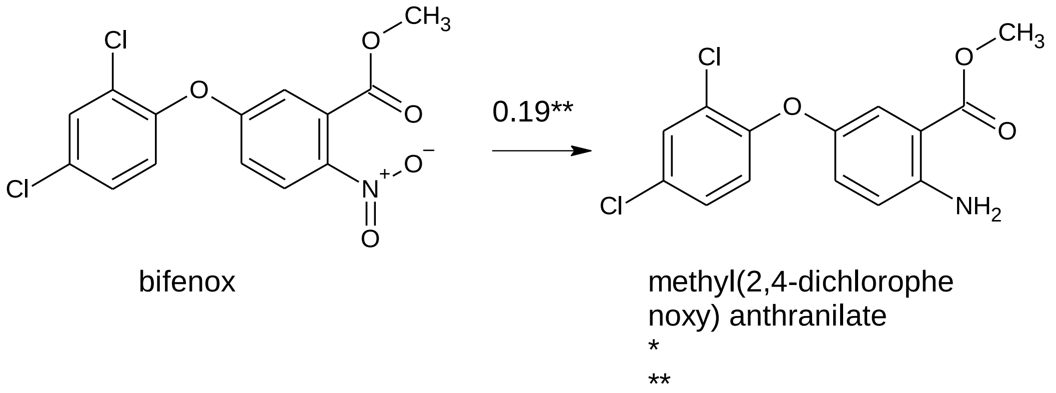


Figure 4.61. Degradation scheme of bifenox (Leather, 1975*; Roy et al., 2004**). Number on arrow indicates fraction of formation of TP from the parent compound.

4.14.2 Physicochemical Properties for Bifenox Family

Compiled literature derived physicochemical property, EPI Suite estimated ones for parent compound, and TP are presented in Appendix A-Table A1. FAVs for parent chemical and its TP are given in Appendix A- Table A2.

4.14.3 Evaluation and Persistency of Bifenox Family

Table 4.33 indicates the environmental mass distribution of the bifenox family, total mass, and persistence. Sediment is the main environmental compartment for bifenox when we exclude bifenox emission into water media. Intermedia transport mechanisms from water to sediment by diffusion and sediment deposition are considerable for bifenox when compared to its TP. While water is the second prominent compartment for bifenox, it becomes the primary sink compartment for methyl (2, 4-dichlorophenoxy) anthranilate. Contrary to bifenox, its TP does not accumulate in air medium and a lower amount can be observed in sediment medium. Hence, the mobility of bifenox could increase as it turns into methyl (2, 4-dichlorophenoxy) anthranilate.

Table 4.33. Amount of bifenox & its TP as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	In sediment (%)	Total (kg)	Persistence (hour)
Bifenox	Air	1.50E+05	17	1.88E+05	22	1.12E+05	13	4.11E+05	48	8.61E+05	861
	Water	7.18E+03	0	1.60E+06	31	5.37E+03	0	3.51E+06	68	5.12E+06	5120
	Soil	5.03E+00	0	2.20E+02	0	2.42E+05	100	4.82E+02	0	2.43E+05	243
	All three	5.24E+04	3	5.96E+05	29	1.20E+05	6	1.31E+06	63	2.07E+06	2075
Methyl(2,4-dichlorophenoxy) anthranilate	Air	0.00E+00	0	3.15E+05	66	1.59E+05	34	6.17E+02	0	4.75E+05	2500
	Water	0.00E+00	0	3.95E+05	100	0.00E+00	0	7.73E+02	0	3.95E+05	2082
	Soil	0.00E+00	0	3.06E+05	63	1.77E+05	37	6.00E+02	0	4.84E+05	2546
	All three	0.00E+00	0	3.39E+05	75	1.12E+05	25	6.63E+02	0	4.51E+05	2376

Based on Table 4.33, the environmental mass of compounds was plotted regarding several media along with various emission scenarios in Figure 4.62. Bifenox emission into only soil and the methyl (2, 4-dichlorophenoxy) anthranilate emission into only water medium explains the highest amount of bifenox and its TP in soil and water, respectively. Also, intermedia transport from water to sediment could be an important mechanism for bifenox.

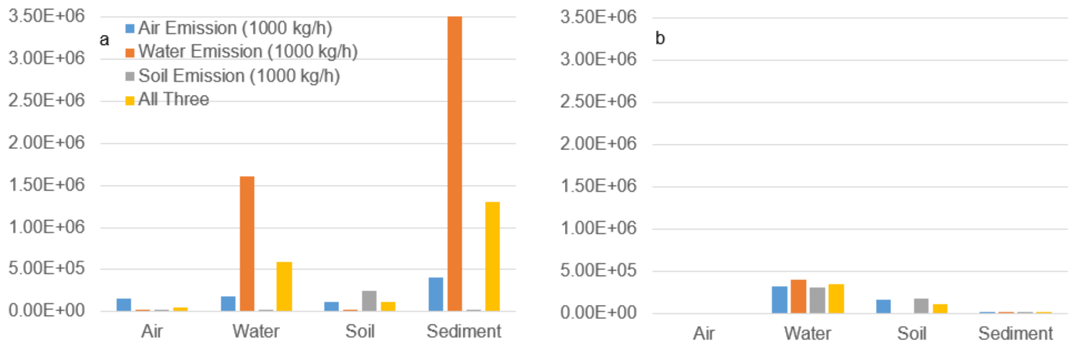


Figure 4.62. Amount (kg) of (a) bifenox, and (b) methyl (2, 4- dichlorophenoxy) anthranilate in the environment.

Individual persistence of bifenox and its TP, together with their joint persistence are represented in Figure 4.63. From the figure, the persistence of bifenox is increased when the degradation product is taken into consideration. Even if the persistence of the degradation product is higher than the main compound, joint persistence is lower than the threshold value that was stated as 100 days. Either bifenox or its TP could not be a concern as compared to the persistence of other priority chemicals and their TPs.

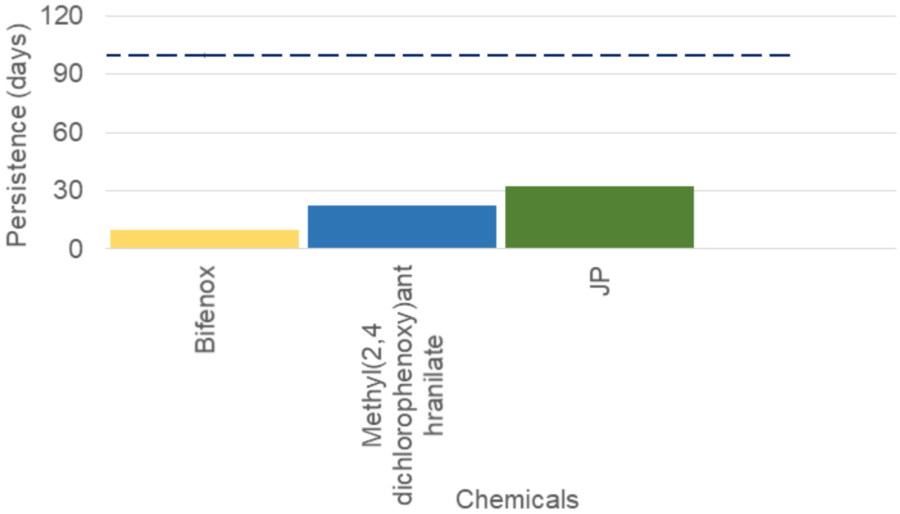


Figure 4.63. Persistence of bifenox family with a dashed line that is P_{ov} criterion of 100 days (Webster et al., 1998).

The predictive capability of EPI Suite and the effects of physicochemical inputs on chemical amount and persistence is demonstrated in Table 4.34. The percentage differences between EPI Suite predicted and the FAV is changing from two significant figures to four significant figures. However, only -1614% difference in two soil half-lives causes a 94% increase in percent difference between the outputs. Hence, half-life in soil should be determined carefully as much as possible.

Table 4.34. Effect of FAV and EPI Suite predicted inputs on bifenox amount and persistence with percentage difference.

Chem	FAV	EPI Suite Value	Diff. Btw Inputs as %	Chem Amount (mole)	Persistence (d)	Percent Diff (%)
bifenox				7.11E+05	10	
bifenoxmeltpred	8.50E+01	1.77E+02	-108	7.11E+05	10	0
bifenoxvaporpred	3.20E-04	1.42E-05	96	7.11E+05	10	0
bifenoxsolpred	3.50E-01	5.77E+00	-1549	7.11E+05	10	0
bifenoxhenrypred	3.13E-01	8.42E-04	100	7.11E+05	10	0
bifenoxsoilpred	1.68E+02	2.88E+03	-1614	1.22E+07	173	94
bifenoxlogKowpred	4.84E+00	3.81E+00	21	7.11E+05	10	0
bifenoxKocpred	2.29E+04	3.68E+03	84	7.13E+05	10	0
bifenoxpredicted				1.21E+07	172	94

Sensitivity analysis for bifenox family is shown in Figure 4.64. According to this figure, when half-life in soil is the most sensitive physicochemical input for bifenox, it is the second sensitive parameter for its TP. Since half-life in water is the most sensitive parameter for its TP.

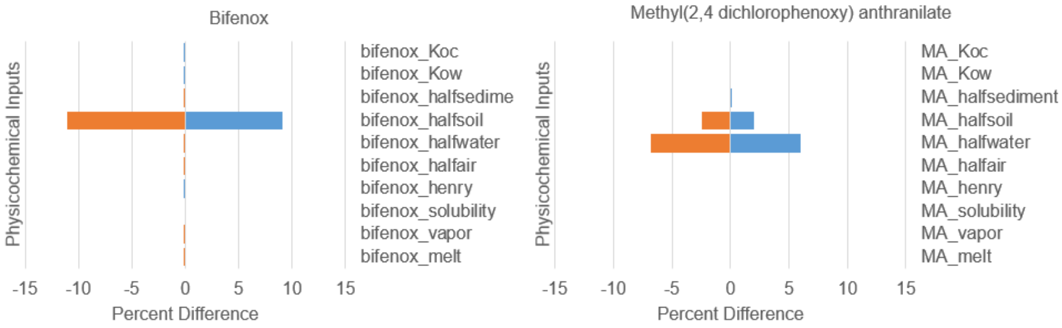


Figure 4.64. Sensitivity analysis results for bifenox and methyl (2, 4-dichlorophenoxy) anthranilate.

4.15 Hexachlorobutadiene (HCBD)

As an unintentional by-product during the production of chlorinated solvents, hexachlorobutadiene (HCBD) is a halogenated hydrocarbon. According to the Stockholm Convention, HCBD was listed among the persistent organic pollutants in 2015. Because of its toxicity and long-range transportability, it is a candidate for Arctic contamination (Balmer et al., 2019). Also, hydrophobic and volatile characteristics of HCBD causes volatilization to air or deposition into the sediment (USEPA, 1980). Chronic exposure to HCBD leads to form action of kidney tumors. In addition, it has adverse respiratory, and developmental effects on rats (ATSDR, 2019).

4.15.1 Degradation Pathway Scheme for Hexachlorobutadiene

HCBD could reductively dechlorinated to pentachlorobutadiene and tetrachlorobutadiene by the action of anaerobic microorganisms. HCBD is reduced by consecutive stages, so one chlorine atom is replaced by one hydrogen atom at each step. This type of transformation was determined in sediment samples. 1,2,3,4-TeCBD is one of the end products of HCBD degradation. Furthermore, PCBD is the first intermediate before the formation of an end product, namely 1, 2, 3, 4-TeCBD (Bosma et al., 1994). Therefore, these two TPs were investigated with respect to persistence. The degradation scheme of HCBD is represented in Figure 4.65.

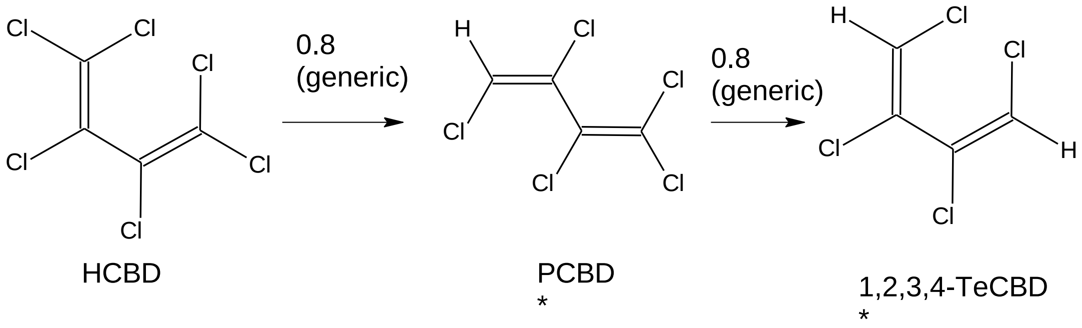


Figure 4.65. Degradation scheme of HCBD (Bosma et al., 1994*). Number on each arrow indicates the fraction of formation of TPs.

4.15.2 Physicochemical Properties for Hexachlorobutadiene Family

Compiled literature derived physicochemical property, EPI Suite estimated ones for parent compound, and TPs are presented in Appendix A-Table A1. FAVs for parent chemical and its TPs are given in Appendix A- Table A2.

4.15.3 Evaluation and Persistency of Hexachlorobutadiene

Table 4.35 indicates the environmental mass distribution of the substance family, total mass, and persistence. All members of this family predominantly prefer the air phase, with low amounts in the rest of the different media. This is consistent with HCBD’s high vapor pressure and K_{aw}. The half-life in air for HCBD with 8530 hours is the highest (except methane) among all the compounds evaluated in this study. The TPs of HCBD have lower half-lives and higher vapor pressure, so they prefer the air phase but are degraded much faster than HCBD. Hence, the last column of Table 4.35 shows smaller persistence for PCBD and TeCBD.

Table 4.35. Amount of HCBD & its TPs as kg and percent in different environmental compartments and persistence.

Chem	Emission Medium	In air (kg)	In air (%)	In water (kg)	In water (%)	In soil (kg)	In soil (%)	In sediment (kg)	sediment (%)	Total (kg)	Persistence (hour)
HCBD	Air	1.22E+07	99	4.06E+04	0	7.79E+04	1	2.97E+03	0	1.23E+07	12273
	Water	1.14E+07	96	4.21E+05	4	7.31E+04	1	3.08E+04	0	1.19E+07	11923
	Soil	1.18E+07	96	4.11E+04	0	4.27E+05	3	3.00E+03	0	1.23E+07	12277
	All three	1.18E+07	97	1.68E+05	1	1.93E+05	2	1.23E+04	0	1.22E+07	12157
PCBD	Air	2.52E+06	99	7.13E+03	0	9.68E+03	0	2.57E+02	0	2.54E+06	3173
	Water	2.11E+06	88	2.78E+05	12	8.09E+03	0	1.00E+04	0	2.40E+06	3004
	Soil	2.39E+06	93	7.84E+03	0	1.79E+05	7	2.82E+02	0	2.58E+06	3222
	All three	2.34E+06	93	9.77E+04	4	6.55E+04	3	3.52E+03	0	2.51E+06	3133
TeCBD	Air	4.65E+05	99	1.56E+03	0	1.39E+03	0	3.47E+01	0	4.68E+05	731
	Water	3.88E+05	63	2.20E+05	36	1.16E+03	0	4.89E+03	1	6.14E+05	959
	Soil	4.46E+05	80	2.54E+03	0	1.07E+05	19	5.65E+01	0	5.55E+05	868
	All three	4.33E+05	79	7.46E+04	14	3.65E+04	7	1.66E+03	0	5.46E+05	853

Based on Table 4.35, the environmental mass of compounds was plotted in several media under various emission scenarios in Figure 4.66.

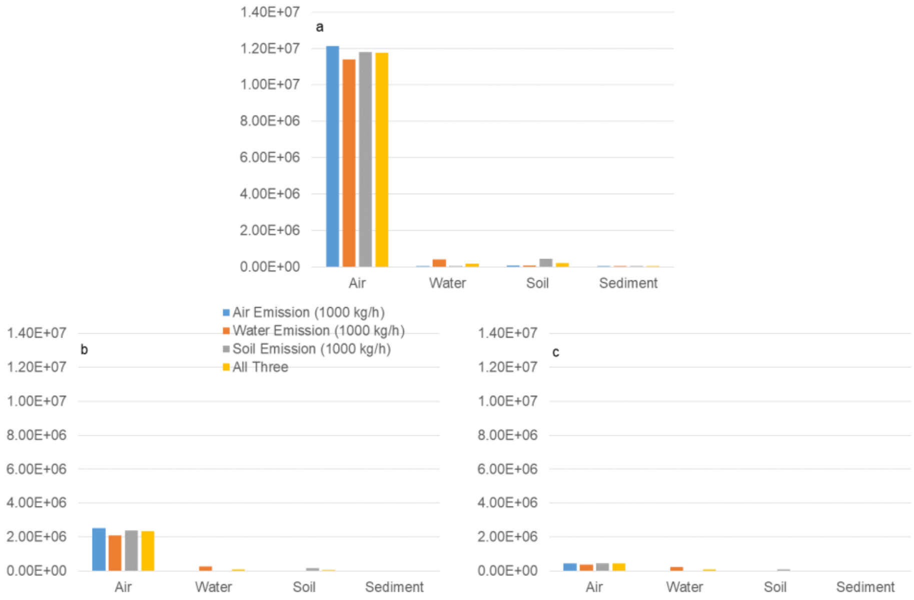


Figure 4.66. Amount (kg) of (a) HCBD, (b) PCBD, (c) TeCBD in the environment.

Individual persistence of HCBD and its TPs, together with their joint persistence are represented in Figure 4.67. The figure is presented for air as the mode-of-entry because air is the dominant medium for HCBD and the most probable pathway of entry into the environment. This figure is consistent with the aforementioned discussion on the very high half-life in air, HCBD's persistence is much higher when compared to the TPs. Nevertheless, considering PCBD and the end-product of TeCBD does contribute to an increased joint persistence for HCBD.

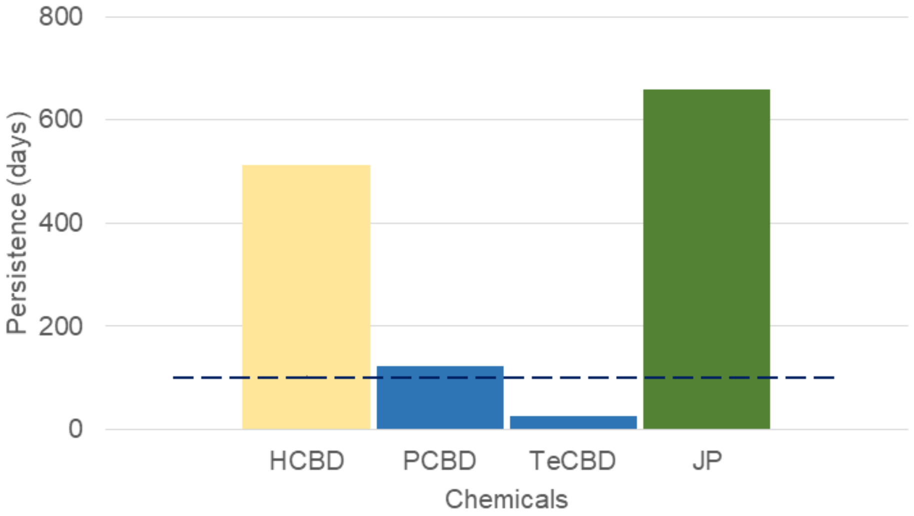


Figure 4.67. Persistence of HCBD family with a dashed line that is overall persistence criterion (P_{ov}) of 100 days (Webster et al., 1998).

The predictive capability of EPI Suite and the effects of physicochemical inputs on chemical amount and persistence can be understood in Table 4.36. None of the differences between FAV and EPI Suite predicted values result in a change of the predicted persistence. A much smaller number of physicochemical parameters could be tested for HCBD because of the data availability for HCBD. Those not shown in the table were predicted using the EPI Suite.

Table 4.36. Effect of FAV and EPI Suite predicted inputs on HCBD amount and persistence with percentage difference.

Chem	FAV	EPI Suite Value	Diff. Btw Inputs as %	Chem Amount (mole)	Persistence (d)	Percent Diff (%)
HCBD				4.71E+07	511	
HCBDmeltpred	-2.10E+01	-6.20E+00	70	4.71E+07	511	0
HCBDvaporpred	2.36E+01	2.84E+01	-20	4.71E+07	511	0
HCBDsolubpred	4.34E+00	5.74E+00	-32	4.71E+07	511	0
HCBDHenrypred	1.42E+03	1.29E+03	9	4.71E+07	511	0
HCBDKowpred	4.76E+00	4.72E+00	1	4.71E+07	511	0
HCBDpredicted				4.71E+07	511	0

The sensitivity analysis for the HCBD family is represented in Figure 4.68. According to this figure, half-life in the air is the most sensitive parameter for all members. This is consistent with the high partitioning of all members of the family in air medium.

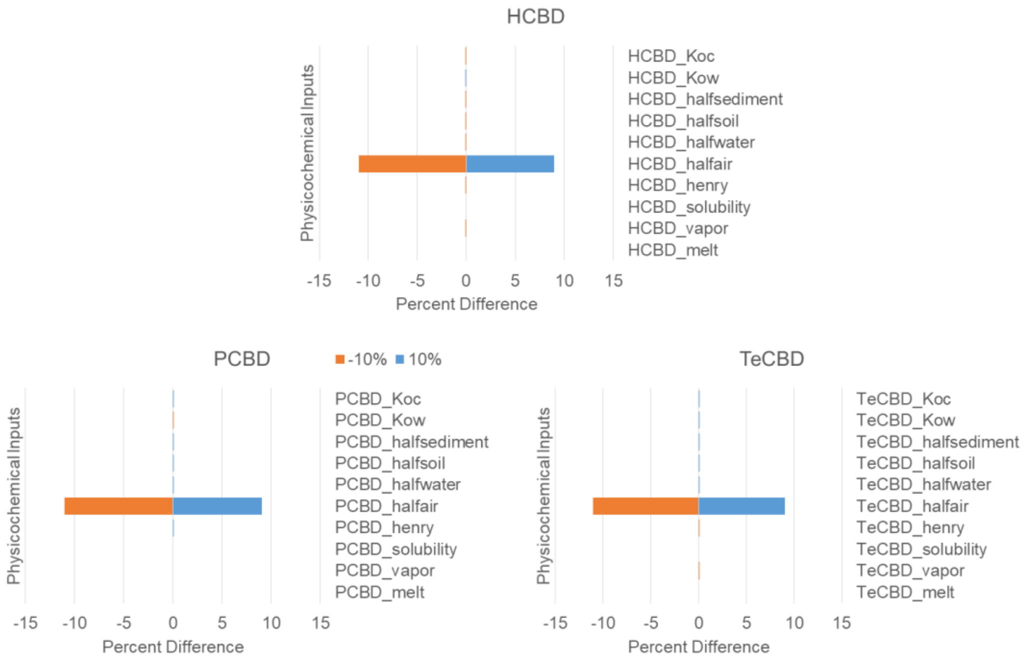


Figure 4.68. Sensitivity analysis results for HCBD and its TPs, namely, PCBD, and TeCBD.

4.16 Overall Evaluation of Results

In this study, TPs of the selected priority pollutants were compiled from laboratory or field studies investigating the presence of TPs in natural or engineered treatment systems. Metabolites identified by in vivo studies, i.e. those using prediction software were excluded on purpose. Experimentally obtained physicochemical properties from respectable resources (i.e. Mackay et al., 2006) were used as much as possible; however, for most of the TPs, EPI Suite prediction tool had to be used due to unavailability of information. To obtain input data for EPI Suite, articles that include the molecular structure of parent compounds and their TPs were considered. Main TPs and stable end products were included in degradation schemes as much as possible.

For all studied main compounds, i.e. priority pollutants, a 1000 kg/h emission rate was assumed. For p,p'-DDT, because it is an impurity of the priority pollutant, dicofol, this was not the case. An emission rate corresponding to its weight percentage as the impurity of dicofol was used (i.e. 18 kg/h) for p,p'-DDT. For the mass of all compounds in various media, four emission scenarios, namely, emission into only air, only water, only soil, and all media at the same time were tested. Under simultaneous emissions to air, water, and soil scenario (at 1000 kg/h each), environmental mass distribution in several media was found by dividing EQC results into three (i.e. to be able to compare 3000 kg/h as the sum to all media with 1000 kg/h to a single medium). This way, an equal basis comparison could be made with emission into a single medium.

During the calculation of PP, SP, and JP, FAV vs. EPI Suite results comparison table, and sensitivity analysis, emission into the same medium were considered. The selection of the mode-of-entry for the aforementioned calculations was based on the use of the chemical. For example, for pesticides, since they are intentionally applied on soil, selected mode-of-entry was selected as 100% soil. For others, however, i.e. trichloromethane and HCBD, highly volatile compounds, were assumed to be introduced into the evaluative environment via 100% air.

For all the studied compounds, TPs were assumed to be emitted into the same medium as their parent compounds. In reality, according to the scientific studies from which TP information is obtained, one can see that TPs can be formed in various media, such as water or air. Subsequently, mode-of-entry for TPs could vary from that of their parents, which could in turn have an impact on their persistence in the environment. This constitutes one type of uncertainty on the proposed joint persistences for priority pollutants studied here. Another one is regarding uncertainty of predicted physicochemical property information, and the adjustment that had to be carried out to obtain thermodynamic consistency among related parameters. Furthermore, selection of TPs was based on available scientific literature, so while one TP could be included for a parent priority pollutant, another could have four TPs, including further generations of TPs–which in turn has an impact on the resulting JP. Lastly, selection of different ratios for environmental compartments, incorporation of more compartments or processes such as advection would be expected to have an impact on the PP and JP estimations. Nevertheless, the main findings obtained within the confines of this study are discussed below.

An overall summary table is prepared for all compound families investigated as a part of this study Table 4.37. When results are evaluated, it can be observed that some TPs, namely, DEA, DBF, 4-CBP, BP, PA, lactam, alachlor OXA, TR-4, TR-7, chlorpyrifos oxon, and methane can significantly increase the joint persistence of the priority pollutant. On the other hand, other TPs, namely DDD, DDNU, alachlor ESA, TCP, DCM, and TeCBD do not have a significant contribution to joint persistence.

DEA, which is a transformation product of atrazine, is likely to be observed in soil, groundwater and, surface water (Thomas et al., 1994). Additionally, dissolved organic carbon amount affects DEA formation (Torrents et al., 1997). So, incorporation of DEA into the persistence of atrazine via JP, as proposed in this study, would be valuable. A similar conclusion was made by Gasser et al. (2007).

TPs of dicofol which are DBF, 4-CBP, and BP have more contribution to joint persistence when compared to the parent compound. However, the JP of dicofol family might generate a concern for only water and sediment media due to their expected discharge from wastewater treatment plants (WWTPs). These TPs form under photocatalytic conditions (Yu et al., 2008). Also, sonochemical treatment was proposed as another alternative which results in the formation of TPs from dicofol in WWTPs (Debabrata & Sivakumar, 2018). When their degradation half-lives are evaluated, it is seen that dicofol and all TPs degrades faster in water (i.e. 99, 1440, 900, 360 hrs as can be seen in Appendix A Table A-1) when compared to soil (i.e. 1080, 2880, 1800, 720 hrs). Hence consideration of soil mode-of-entry during JP calculation results in a more conservative persistence estimate for the dicofol family.

PA is also a significantly persistent member of the DEHP family. Bacteria and fungi biodegrade DEHP, resulting in the formation of PA (Magdouli et al., 2013). However, DEHP degradation is not possible to the same extent in various soils because of large heterogeneity and insufficient substrate and mass transfer restrictions (Davis et al., 2003). Therefore, environmental conditions could be especially influential for the persistence of the DEHP family. If PA is not formed, which almost doubles the persistence of DEHP, then JP can be expected to be lower in the environment.

Along with p,p’-DDT, its TPs are observed in the soil medium. Aerobic and anaerobic conditions are favored for the formation of p,p’-DDE, and p,p’-DDD, respectively (Huang et al., 2018). Excluding p,p’-DDE, other TPs do not contribute significantly to joint persistence, according to our study. Lower contribution of TPs to joint persistence was also demonstrated by Schenker et al. (2007). DDD and DDE were found to be less persistent compared to DDT, so their contribution to joint persistence was not stated to be as important as the contribution of DDT (Fenner et al., 2009). By considering the structural similarity between DDT, DDE, and DDD, the lower persistence of DDD was proposed by Fenner et al. (2009) to be perhaps due to underestimated half-life information.

Despite the high stability of alachlor in water (Peñuela & Barceló, 1996), alachlor OXA and alachlor ESA can occur in surface waters under natural conditions (Graham et al., 1999). While alachlor ESA has the lowest contribution to joint persistence, alachlor OXA has the highest. The high persistence contribution of alachlor OXA might be concerning for the aquatic ecosystem. After alachlor OXA, lactam is the secondly ranked persistent compound. However, it cannot be as problematic as alachlor OXA since the catalysis mechanism is required for lactam formation (Pérez et al., 2018). In this study, all TPs were assumed to be introduced into the soil compartment, which has twice as high predicted half-lives as those in water. Also, lactam may not be observed in the natural environment under non-catalyzed conditions. So, the JP estimation for alachlor proposed in this study can be considered to be a conservative one and expected to be lower in the actual environment.

TR-4 and TR-7 from trifluralin were observed in Fe (II) and goethite mixture at approximately neutral pH. These TPs were detected in soil and sediments (Klupinski & Chin, 2003). They are observed to have a significant influence on the JP of trifluralin. Considering that there is a good chance these TPs can be formed under natural environmental conditions; their monitoring is recommended as a result of our findings.

Regarding the chlorpyrifos family, although both TPs have similar secondary persistence, CPO has a much higher contribution to JP when compared to TCP. This is because 89% of chlorpyrifos is converted into CPO while only 2% is converted to TCP (as suggested by (Duirk & Collette, 2006). Both TPs, (i.e. CPO and TCP) occur via biotransformation (Pradeep & Subbaiah, 2015) depending on moisture, temperature, organic matter (Supreeth & Raju, 2017), and the presence of degradative microorganisms. Thus, it can be stated that there is a good chance CPO might be an important TP under environmental conditions. Additionally, CPO and TCP can be present in the natural aquatic ecosystem because of discharge from water treatment plants (Duirk & Collette, 2006). Therefore, it is suggested as a result of the present study, both TPs need to be monitored and chlorpyrifos is regarded as a contaminant with a potentially higher persistence when compared to its primary persistence.

Chlorinated methanes were deemed among the most prominent pollutants in soil and groundwater (Lien & Zhang, 1999). As is discussed in the relevant section, methane and DCM are two TPs from trichloromethane transformation. Due to the extremely persistent nature of methane, it has the highest contribution to joint persistence, when compared to DCM. It should be noted, however, that both TPs occur under the action of the Pd/Al catalyst (Lowry & Reinhard, 1999). Hence, they are not likely to be encountered as natural degradation products of trichloromethane in the environment. Subsequently, consideration of primary persistence, rather than joint persistence of trichloromethane is proposed.

Hexachlorobutadiene reductively dechlorinates into 1, 2, 3, 4-TeCBD via anaerobic microorganisms along with titanium (III) citrate and hydroxo-cobalamin in sediment medium (Bosma et al., 1994). Although this degradation mechanism can likely take place in the environment, 1, 2, 3, 4-TeCBD does not have a substantial contribution to the joint persistence of the hexachlorobutadiene family. Furthermore, all members of this family are likely to partition into the gaseous phase and hence their persistence could be dominated by gaseous reactive processes.

As a result of the comparison of FAV versus EPI Suite predicted values, as well as sensitivity analyses, degradation half-lives come up as the most influential on the P_{ov} of compounds. Depending on the medium the compound partitions in, the careful selection and/or prediction of these half-lives are crucial. For example, for BDE-153, if half-life in sediment was taken from Zhu et al. (2014) (which is on the order of thousands of hrs), it would have a much smaller abundance in sediment, when compared to the use of sediment half-life from EPI Suite (which is on the order of tens of thousands of hrs). Subsequently, half-life in water should be determined carefully for atrazine. On the other hand, half-life in soil should be selected meticulously for p, p’-DDT, DEHP, alachlor, trifluralin, chlorpyrifos, and bifenox.

Lastly, an issue that was encountered via use of the EQC model needs to be mentioned here. As explained previously, the EQC model is based on the fugacity concept that was integrated into the chemical fate modeling by Mackay (1979) and described in detail in the book by Mackay (2001). According to Mackay et al. (1996b), compounds to be modeled are divided into five types. Type 1 is the category for most organic chemicals where fugacity is measurable in all phases because compounds are considered “multimedia”. On the other hand, Type 2 compounds are cations, anions and non-volative organic chemicals. For Type 2 chemicals, fugacity is zero in air phase but measurable in all other phases, and equilibrium criterion is defined by a concept called aquivalence, i.e. equivalent aqueous concentration. The rest of the types are Type 3: very hydrophobic, Type 4: large molecular weight, metals, inorganics and Type 5: organo-metals and phenols of low pKa.

We believe a number of our parent compounds and TPs fall under Type 2 category (see Table 4.38 below for a complete list). Hughes et al. (2012) emphasize that the EQC model handles Type 1, 2 and 3 chemicals as a single class, so ideally, there should be no problem associated with the results of the EQC model for these chemicals. Even though this is the case, outputs for these chemicals, especially when water is the mode-of-entry, shows a very large percent of the mass of compound remaining in the water phase. Sometimes, the percentage in the water phase cannot be justified by the very low solubility of the compound. This can be seen from the % distribution difference between equilibrium (Level II) and non-equilibrium (Level III) mass distribution of compounds in Table 4.38. This situation stems from the fact that Level III is a non-equilibrium distribution and when air fugacity is taken as zero and no transfer from or into air phase is present, the compound transfer from the water phase becomes rather limited and slow, resulting in a very large presence in the water phase. We observe this situation for compounds that have extremely low K_{aw} values (i.e. less than around 10^{-7}) and very low VP values (i.e. less than around 10^{-5} Pa), coinciding with low solubilities (i.e. less than approximately 100 g/m^3).

In a number of the instances during sensitivity analysis, we encountered unexpected sensitivity towards change in VP, and interestingly only VP. We believe the reason for this is also somewhat associated with the aforementioned compound types, Type 1 and 2. When we change the VP slightly (i.e. 10% increase or decrease), the model yields a significantly different environmental distribution than the original one, possibly via use of aquivalence approach rather than fugacity approach. Users of the EQC model are therefore warned regarding the modeling of compounds that have very small VP (i.e. $< 10^{-5}$ Pa), very small K_{aw} (i.e. $< 10^{-7}$) and low solubility (i.e. $<10^{2}$ g/m^{3}). The issue becomes especially elevated when we compare a family of compounds with each other, rather than an individual evaluation of one compound in and of itself. Another explanation for unexpected results in sensitivity analysis could be due to improperly estimated EPI Suite half-lives in environmental compartments. However, correspondence with model developers is under way for further elucidation of this issue.

Table 4.37 Overall results of individual and joint persistence as well as environmental distribution of selected priority pollutants and their TPs considering only one main mode-of-entry.

Compound family	Fraction of formation ff^{xy}	Mode-of-entry	% mass in air	% mass in water	% mass in soil	% mass in sediment	Persistence (d)	Joint Persistence (d)	JP/PP
Aclonifen		Soil	0	0	100	0	166	226	1.4
TP1Acl	0.8	Soil	0	52	48	0	60		
Alachlor		Soil	0	5	95	0	22	109	5
Alachlor OXA	0.49	Soil	0	33	67	0	43		
Alachlor ESA	0.11	Soil	0	52	48	0	7		
Lactam	0.32	Soil	0	7	93	0	38		
Atrazine		Soil	0	40	60	0	56	202	3.6
DEA	0.5	Soil	0	27	73	0	79		
DIA	0.3	Soil	0	33	66	0	45		
HA	0.2	Soil	0	13	87	0	22		
BDE-153		Soil	0	0	99	1	522	1663	3.2
BDE-101	0.36	Soil	0	0	99	1	215		
BDE-99	0.37	Soil	0	0	99	1	219		
BDE-118	0.27	Soil	0	0	99	1	159		
BDE-52	0.4	Soil	0	0	99	1	99		
BDE-49	0.4 & 0.27	Soil	0	0	99	1	166		
BDE-47	0.27	Soil	0	0	99	1	67		
BDE-66	0.4 &0.27	Soil	0	0	99	1	141		
BDE-77	0.4	Soil	0	0	99	1	74		

Table 4.37. (Cont‘d)

Compound family	Fraction of formation ff^{xy}	Mode-of-entry	% mass in air	% mass in water	% mass in soil	% mass in sediment	Persistence (d)	Joint Persistence (d)	JP/PP
Bifenox		Soil	0	0	100	0	10	32	3.2
TPBifenox	0.19	Soil	0	63	37	0	22		
CFVP		Soil	0	0	100	0	231	557	2.4
Desethyl-CFVP	0.8	Soil	0	63	37	0	92		
2,4-dichlorophenacyl chloride	0.8	Soil	0	7	93	0	163		
1-(2,4-dichlorophenyl) ethane-1,2-diol	0.8	Soil	0	37	63	0	70		
Chlorpyrifos		Soil	0	0	100	0	43	201	4.6
CPO oxon	0.89	Soil	0	6	94	0	153		
TCP	0.02	Soil	0	5	95	0	5		
p,p’-DDT		Soil	0	0	99	1	1027	1941	1.6
p,p’-DDE	0.65	Soil	0	0	99	0	894		
p,p’-DDD	0.01	Soil	0	0	99	1	11		
p,p’-DDNU	0.04	Soil	0	0	100	0	9		
DEHP		Soil	0	0	100	0	33	118	3.6
MEHP	0.8	Soil	0	0	100	0	35		
PA	0.8	Soil	0	30	70	0	50		
Dicofol		Soil	0	11	89	0	32	369	11.7
DBF	0.75	Soil	0	2	98	0	188		
4-CBP	0.8	Soil	0	2	98	0	108		
BP	0.8	Soil	0	1	99	0	42		

Table 4.37. (Cont‘d)

Compound family	Fraction of formation ff^{xy}	Mode-of-entry	% mass in air	% mass in water	% mass in soil	% mass in sediment	Persistence (d)	Joint Persistence (d)	JP/PP
Diuron		Soil	0	56	43	0	83	253	3
DCPMU	0.4	Soil	0	3	97	0	45		
MCPDMU	0.4	Soil	0	5	95	0	48		
DCPU	0.8	Soil	0	4	96	0	38		
DCA	0.8	Soil	0	2	98	0	39		
HCBD		Air	99	0	1	0	511	660	1.3
PCBD	0.8	Air	99	0	0	0	122		
TeCBD	0.8	Air	99	0	0	0	26		
PeCB		Soil	1	0	99	0	513	1080	2
1,2,3,5-TeCB	0.91	Soil	1	0	99	0	181		
1,2,4,5-TeCB	0.09	Soil	1	0	99	0	18		
1,3,5-TCB	0.93	Soil	1	0	99	0	195		
1,2,4-TCB	0.07 & 1	Soil	1	0	99	0	35		
1,3-DCB	1	Soil	3	0	97	0	137		
TCM		Air	99	1	0	0	102	10783	105
DCM	0.17	Air	99	1	0	0	24		
Methane	0.7	Air	100	0	0	0	10657		
Trifluralin		Soil	0	0	100	0	102	864	8.5
TR-4	0.71	Soil	0	1	98	1	402		
TR-7	0.82	Soil	0	84	16	0	281		
TR-9	0.27	Soil	0	4	96	0	80		

Table 4.38. Examples of EQC Level III and II results for species (possibly exhibiting Type 2 character) showing significantly different water phase distribution when mode-of-entry is water.

		In air				In Water				In soil				In sediment				Total	
Chem	**Emission Medium in Level III**	**kg Level III**	**kg Level II**	**% Level III**	**% Level II**	**kg Level III**	**kg Level II**	**% Level III**	**% Level II**	**kg Level III**	**kg Level II**	**% Level III**	**% Level II**	**kg Level III**	**kg Level II**	**% Level III**	**% Level II**	**kg Level III**	**kg Level II**
Atrazine	Air	0.00E+00		0		5.59E+05		43		7.25E+05		56		9.61E+02		0		1.28E+06	
	Water	0.00E+00	4.28E+01	0	0	7.93E+05	7.36E+05	100	82	0.00E+00	1.59E+05	0	18	1.36E+03	3.53E+03	0	0	7.95E+05	8.99E+05
	Soil	0.00E+00		0		5.33E+05		40		8.06E+05		60		9.16E+02		0		1.34E+06	
	All three	0.00E+00		0		6.28E+05		55		5.10E+05		45		1.08E+03		0		1.14E+06	
Diuron	Air	0.00E+00		0		1.17E+06		60		7.80E+05		40		1.89E+03		0		1.95E+06	
	Water	0.00E+00	1.33E+02	0	0	1.56E+06	1.04E+06	100	53	0.00E+00	8.97E+05	0	46	2.51E+03	1.99E+04	0	1	1.56E+06	1.96E+06
	Soil	0.00E+00		0		1.13E+06		56		8.66E+05		43		1.82E+03		0		1.99E+06	
	All three	0.00E+00		0		1.28E+06		70		5.49E+05		30		2.07E+03		0		1.84E+06	
Dicofol	Air	0.00E+00		0		8.69E+04		12		6.10E+05		88		1.73E+02		0		6.97E+05	
	Water	0.00E+00	9.85E-01	0	0	1.43E+05	1.14E+04	100	8	0.00E+00	1.23E+05	0	90	2.84E+02	2.74E+03	0	2	1.43E+05	1.37E+05
	Soil	0.00E+00		0		8.07E+04		11		6.78E+05		89		1.60E+02		0		7.59E+05	
	All three	0.00E+00		0		1.03E+05		19		4.29E+05		81		2.06E+02		0		5.33E+05	
Alachlor ESA	Air	0.00E+00		0		1.01E+05		56		8.05E+04		44		1.96E+02		0		1.82E+05	
	Water	0.00E+00	2.16E-06	0	0	1.42E+05	1.39E+05	100	97	0.00E+00	3.72E+03	0	3	2.74E+02	8.27E+01	0	0	1.42E+05	1.43E+05
	Soil	0.00E+00		0		9.68E+04		52		8.95E+04		48		1.87E+02		0		1.86E+05	
	All three	0.00E+00		0		1.13E+05		67		5.67E+04		33		2.19E+02		0		1.70E+05	
TP1Acl	Air	0.00E+00		0		7.43E+05		56		5.91E+05		44		1.44E+03		0		1.34E+06	
	Water	0.00E+00	8.29E-04	0	0	1.04E+06	4.04E+05	100	24	0.00E+00	1.26E+06	0	74	2.01E+03	2.81E+04	0	2	1.04E+06	1.70E+06
	Soil	0.00E+00		0		7.10E+05		52		6.57E+05		48		1.37E+03		0		1.37E+06	
	All three	0.00E+00		0		8.31E+05		67		4.16E+05		33		1.61E+03		0		1.25E+06	
PA	Air	0.00E+00		0		1.72E+05		35		3.21E+05		65		3.17E+02		0		4.93E+05	
	Water	0.00E+00	2.02E-02	0	0	3.32E+05	3.30E+05	100	98	0.00E+00	5.76E+03	0	2	6.12E+02	1.28E+02	0	0	3.33E+05	3.35E+05
	Soil	0.00E+00		0		1.54E+05		30		3.56E+05		70		2.84E+02		0		5.11E+05	
	All three	0.00E+00		0		2.20E+05		49		2.26E+05		51		4.05E+02		0		4.46E+05	
Desethyl-Chlorfenvinphos	Air	0.00E+00		0		1.33E+06		66		6.70E+05		34		2.60E+03		0		2.00E+06	
	Water	0.00E+00	3.86E+00	0	0	1.66E+06	1.60E+06	100	93	0.00E+00	1.22E+05	0	7	3.25E+03	2.72E+03	0	0	1.67E+06	1.73E+06
	Soil	0.00E+00		0		1.29E+06		63		7.45E+05		37		2.53E+03		0		2.04E+06	
	All three	0.00E+00		0		1.43E+06		75		4.72E+05		25		2.79E+03		0		1.90E+06	
Methy(2,4-dichlorophenoxy) anthranilate	Air	0.00E+00		0		3.15E+05		66		1.59E+05		34		6.17E+02		0		4.75E+05	
	Water	0.00E+00	6.95E-01	0	0	3.95E+05	4.54E+04	100	6	0.00E+00	6.95E+05	0	92	7.73E+02	1.55E+04	0	2	3.95E+05	7.56E+05
	Soil	0.00E+00		0		3.06E+05		63		1.77E+05		37		6.00E+02		0		4.84E+05	
	All three	0.00E+00		0		3.39E+05		75		1.12E+05		25		6.63E+02		0		4.51E+05	
TR-7	Air	0.00E+00		0		4.68E+06		85		8.03E+05		15		9.30E+03		0		5.49E+06	
	Water	0.00E+00	5.22E-01	0	0	5.08E+06	2.02E+03	100	0	0.00E+00	1.11E+06	0	98	1.01E+04	2.47E+04	0	2	5.09E+06	1.14E+06
	Soil	0.00E+00		0		4.64E+06		84		8.93E+05		16		9.21E+03		0		5.54E+06	
	All three	0.00E+00		0		4.80E+06		89		5.65E+05		11		9.53E+03		0		5.37E+06	

CHAPTER 5

CONCLUSIONS

By considering primary persistence, selected compounds are ranked from the highest to the least one as follows p, p’-DDT, BDE-153, pentachlorobenzene, HCBD, chlorfenvinphos, aclonifen, trichloromethane, trifluralin, diuron, atrazine, chlorpyrifos, DEHP, dicofol, alachlor, and bifenox.

Comparison between the environmental distribution of parent compounds and their TPs indicates that TPs could have a different fate than their parent compounds such as aclonifen versus its TP, chlorfenvinphos versus desethyl-chlorfenvinphos, diuron versus its all TPs, and trifluralin versus TR-7.

A higher chemical amount was detected in the emitted medium, so the mode-of-entry effect was observed. For soil mode-of-entry, amounts of all compounds are the highest in soil media excluding diuron, alachlor ESA, TR-7, desethyl-chlorfenvinphos, TP of aclonifen, and TP of bifenox. For air mode-of-entry, amounts of trichloromethane and hexachlorobutadiene in the air phase are the highest ones.

As expected, many chemicals are likely to stay in the soil phase. Run-off from soil to water could be the reason why the chemical amount in the water medium is higher than the soil medium or the highest for some compounds. Advection elimination from the generic environment gave the opportunity to evaluate the importance of degradation mechanisms in various environmental compartments. In brief, degradation in soil and water are two main loss mechanisms for many of the selected chemicals in this study.

When a 10 % decrease and increase are considered together, half-life in soil, and water are significant chemical-specific physicochemical inputs for all compounds excluding trichloromethane and hexachlorobutadiene.

The ratio of joint persistence to primary persistence for trichloromethane is 105, so it is the most highly affected compound from including TPs into persistence assessment. Dicofol, trifluralin, and alachlor are also highly affected compounds from the persistence of their TPs. On the other hand, HCBD, aclonifen, and p, p'-DDT are not influenced importantly by the presence of their TPs.

This study could be promising when updating monitoring lists considering integrated persistency evaluation of priority pollutants. TPs, namely DEA, DBF, 4-CBP, BP, PA, lactam, alachlor OXA, TR-4, TR-7, chlorpyrifos oxon, and methane can significantly increase the joint persistence of the priority pollutant. While alachlor OXA and TR-7 examination in surface water media might be more critical, investigation the presence of DEA, chlorpyrifos oxon, lactam, PA, TR-4 in the soil may be more significant.

CHAPTER 6

RECOMMENDATIONS

- For future studies, the degradation pathway of TPs could be standardized. Therefore, TPs that occur only as a result of photolysis, or microbial activity could be selected and investigated in detail.
- Uncertainty analysis could be done to determine an interval for persistence values for parent compounds, TPs, and substance family.
- Discussion of suggested TPs in this study could be coupled with toxicity. Hence, monitoring of TPs could be updated according to such a more comprehensive approach.
- Different levels of the EQC model, namely, Level I, Level II, and Level III results could be compared for compound families.
- Environmental parameters of the EQC model can change, so the effects of environmental parameters on chemical distribution and persistence could be tested.
- The EQC results can be compared with the results of another MM model. Therefore, the influence of the used model on chemical mass distribution could be analyzed.

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APPENDICES

A. Input Tables

Table A1. Compiled literature derived physicochemical property and EPI Suite predicted ones for parent compounds and their TPs.

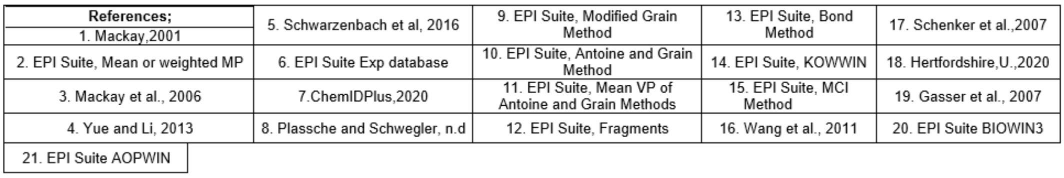
Chemical Name	Molar Mass (g/mol)	Data Temp. C°	Melting Point C°	Ref1	Vapor Pressure (Pa)	Ref2	Solubility in Water (g/m3)	Ref3	Henry's La Constant (Pa*m3/mol)	Ref	t1/2 in air (h)	t1/2 in wate (h)	t1/2 in soil (h)	t1/2 in sediment (h)	LogKov	Ref5	log Ko	Koc (L/kg)	Ref6	Koc Pred.	Modified Koc	Notes
Atrazine	215.7	25	174.0	1	4.00E-05	1	3.00E+01	1	2.88E-04	3	5	550	1700	1700	2.75	1	2.00	1.00E+02	3	2.25E+02		No need to modify Koc
Atrazine (EPI Suite)	215.7	25	113.9	2	3.81E-03	9	4.50E+01	12	4.53E-04	13	9	1440	2880	13000	2.82	14	2.35	2.25E+02	15			Intentional blank
DEA	187.6	25	114.2	2	1.15E-02	9	2.82E+02	12	1.55E-04	13	14	1440	2880	13000	1.51	6	2.02	1.05E+02	15		4.70E+01	Non-ionic TPs from experimentally known parent compound
DIA	173.6	25	112.3	2	2.81E-02	9	5.37E+02	12	1.17E-04	13	29	1440	2880	13000	1.15	6	1.84	6.88E+01	15		3.06E+01	Non-ionic TPs from experimentally known parent compound
HA	197.2	25	133.9	2	1.13E-03	9	3.97E+00	12	6.36E-08	13	9	900	1800	8100	2.09	14	2.26	1.80E+02	15		8.00E+01	Non-ionic TPs from experimentally known parent compound
Diuron	233.1	25	158.0	3	9.20E-05	3	4.00E+01	3	6.83E-04	3	3	1082	2160	1152	2.78	3	2.60	3.98E+02	3	1.09E+02		No need to modify Koc
Diuron (EPI Suite)	233.1	25	126.4	2	6.20E-04	9	1.02E+02	12	5.40E-05	13	24	900	1800	8100	2.67	14	2.04	1.09E+02	15			Intentional blank
DCPMU	219.1	25	123.0	2	2.69E-03	9	2.98E+02	12	2.46E-05	13	25	900	1800	8100	2.46	14	2.06	1.14E+02	15		4.16E+02	Non-ionic TPs from experimentally known parent compound
MCPDMU	198.7	25	107.4	2	6.26E-03	9	4.27E+02	12	7.29E-05	13	8	900	1800	8100	2.03	14	2.24	6.67E+01	15		2.43E+02	Non-ionic TPs from experimentally known parent compound
DCPU	205.0	25	121.9	2	4.34E-03	9	3.95E+02	12	1.12E-05	13	26	900	1800	8100	2.00	14	2.25	9.74E+01	15		3.56E+02	Non-ionic TPs from experimentally known parent compound
DCA	162.0	25	46.2	2	4.09E-01	9	1.35E+03	12	1.06E-01	13	12	900	1800	8100	2.37	14	2.26	1.85E+02	15		6.73E+02	Non-ionic TPs from experimentally known parent compound
Alachlor	269.8	25	40.0	3	2.00E-03	3	2.40E+02	3	2.20E-03	3	12	552	360	48	2.80	3	2.21	1.62E+02	3	3.12E+02		No need to modify Koc
Alachlor (EPI Suite)	269.8	25	128.5	2	2.73E-03	9	4.45E+02	12	2.26E-03	13	6	1440	2880	13000	3.37	14	2.50	3.12E+02	15			Intentional blank
Lactam	233.3	25	130.5	2	6.45E-04	9	1.22E+03	12	2.83E-03	13	5	900	1800	8100	2.60	14	2.23	1.71E+02	15		8.86E+01	Non-ionic TPs from experimentally known parent compound
Alachlor ESA	315.4	25	203.9	2	1.19E-09	9	1.00E+06	12	1.10E-09	13	6	900	1800	8100	1.82	14	1.09	1.24E+01	15		1.24E+00	Ionic TPs from nonionic parent compound
Alachlor OXA	251.3	25	141.6	2	3.10E-06	9	7.71E+04	12	1.00E-03	13	5	900	1800	8100	2.22	14	1.18	1.50E+01	15		7.80E+00	Non-ionic TPs from experimentally known parent compound

Table A1. (Cont'd)

Chemical Name	Molar Mass (g/mol)	Data Temp. C°	Melting Point C°	Ref1	Vapor Pressure (Pa)	Ref2	Solubility in Water (g/m3)	Ref3	Henry's Law Constant (Pa*m3/mol)	Ref4	t1/2 in air (h)	t1/2 in water (h)	t1/2 in soil (h)	t1/2 in sediment (h)	LogKow	Ref5	log Koc	Koc (L/kg)	Ref6	Koc Pred.	Modified Koc	Notes
DEHP	390.5	25	-50.0	1	1.91E-03	5	2.90E-02	5	2.59E+01	5	55	170	550	1700	5.11	1	5.00	1.00E+05	3	1.20E+05		No need to modify Koc
DEHP (EPI Suite)	390.6	25	63.9	2	2.70E-03	9	1.28E-03	12	1.20E+00	13	12	360	720	3240	8.39	14	5.08	1.20E+05	15			Intentional blank
MEHP	390.6	25	63.9	2	2.70E-03	9	1.28E-03	12	1.20E+00	13	12	360	720	3240	8.39	14	5.08	1.20E+05	15		1.20E+04	Anionic product from neutral parent compound
PA	166.1	25	126.6	2	1.02E-04	9	2.97E+04	12	2.21E-07	13	208	360	720	3240	1.07	14	1.91	8.09E+01	15		8.09E+00	Anionic product from neutral parent compound
Dicofol	370.5	25	77.5	3	5.33E-05	3	8.00E-01	3	5.66E-05	3	0	99	1080	38900	3.54	3	3.70	5.01E+03	3	1.27E+04		No need to modify Koc
Dicofol (EPI Suite)	370.5	25	148.3	2	9.18E-06	9	3.07E-01	12	5.67E-05	13	75	4320	8640	38900	5.81	14	4.10	1.27E+04	15			Intentional blank
DBF	251.1	25	107.7	2	8.52E-04	9	7.80E+00	12	1.08E-01	13	103	1440	2880	13000	4.44	14	3.47	2.92E+03	15		1.16E+03	Non-ionic TPs from experimentally known parent compound
4-CBP	216.7	25	91.4	2	1.48E-02	9	3.31E+01	12	1.46E-01	13	85	900	1800	8100	3.79	14	3.26	1.82E+03	15		7.22E+02	Non-ionic TPs from experimentally known parent compound
BP	182.2	25	63.6	2	1.16E-01	9	1.37E+02	12	1.97E-01	13	72	360	720	3240	3.15	14	3.06	1.14E+03	15		4.50E+02	Non-ionic TPs from experimentally known parent compound
DDT	354.5	25	108.5	3	2.00E-05	3	5.50E-03	3	1.31E+00	3	170	5500	17000	55000	6.19	3	5.40	2.51E+05	3	1.69E+05		No need to modify Koc
DDT (EPI Suite)	354.5	25	123.2	2	3.21E-01	9	3.43E-03	12	1.55E+00	13	75	4320	8640	38900	6.79	14	5.23	1.69E+05	15			Intentional blank
DDE	318.0	25	89.0	3	8.66E-04	3	4.00E-02	3	4.20E+00	3	34	10296	20592	38900	5.70	3	5.00	1.00E+05	3			No need to modify Koc because they are experimental
DDD	320.0	25	109.5	3	1.30E-04	3	5.00E-02	3	6.70E-01	3	60	10992	21984	38900	5.50	3	5.00	1.00E+05	3			No need to modify Koc because they are experimental
DDDNU	249.1	25	86.6	2	1.65E-02	9	3.59E-01	12	6.88E+00	13	1	1440	2880	13000	5.15	14	4.60	3.94E+04	15		5.87E+04	Non-ionic TPs from experimentally known parent compound
Trifluralin	335.3	25	49.0	3	2.60E-02	3	5.00E-01	3	4.03E+00	3	170	1700	1700	5500	5.34	3	4.37	2.34E+04	3	1.64E+04		No need to modify Koc
Trifluralin (EPI Suite)	335.3	25	140.0	2	1.80E-03	9	5.50E-02	12	2.15E+01	13	11	4320	8640	38900	5.31	14	4.22	1.64E+04	15			Intentional Blank
TR-4	305.3	25	139.6	2	4.31E-04	9	2.34E-01	12	7.15E-03	13	10	4320	8640	38900	4.58	14	3.71	5.09E+03	15		7.27E+03	Non-ionic TPs from experimentally known parent compound
TR-7	275.3	25	128.2	2	1.18E-03	9	1.97E+00	12	2.93E-05	13	1	4320	8640	38900	3.26	14	3.72	5.25E+03	15		7.51E+03	Non-ionic TPs from experimentally known parent compound
TR-9	191.2	25	106.1	2	1.87E-02	9	8.46E+02	12	2.09E-07	13	1	1440	2880	13000	0.20	14	2.59	3.88E+02	15		5.55E+02	Non-ionic TPs from experimentally known parent compound
Chlorpyrifos	350.6	25	42.0	3	2.27E-03	3	7.30E-01	3	4.72E-01	3	6	576	720	576	4.92	3	3.78	6.03E+03	3	7.28E+03		No need to modify Koc
Chlorpyrifos (EPI Suite)	350.6	25	82.9	2	2.73E-03	9	1.10E+01	12	2.56E-01	13	3	4320	8640	38900	5.11	14		7.28E+03	15			Intentional blank
Chlorpyrifos oxon	334.5	25	83.4	2	8.87E-04	9	2.62E+03	12	5.53E-04	13	7	1440	2880	13000	2.89	14	2.60	3.95E+02	15		3.27E+02	Non-ionic TPs from experimentally known parent compound
TCP	198.4	25	82.3	2	1.38E-01	9	1.25E+02	12	1.91E-03	13	1330	1440	2880	13000	3.01	14	2.94	8.74E+02	15		4.37E+02	Ionic TP from nonionic parent compound
BDE-153	643.6	25	161.5	4	9.46E-06	4	2.57E-02	4	2.37E-01	4	1110	4320	8640	38900	7.48	4	6.54	3.43E+06	16	3.55E+04		
BDE-153 (EPI Suite)	643.6	25	197.1	2	3.83E-07	9	2.07E-03	12	4.77E-02	13	1110	4320	8640	38900	8.55	14	4.55	3.55E+04	15			
BDE-101	564.7	25	182.8	2	6.44E-05	4	5.57E-02	4	6.52E-01	4	493	4320	8640	38900	7.11	4	4.34	2.17E+04	15			No need this part because all compounds including parent compound is estimated
BDE-99	564.7	25	92.5	4	7.53E-05	4	5.70E-02	4	7.43E-01	4	467	4320	8640	38900	7.12	4	6.41	2.56E+06	16			
BDE-118	564.7	25	182.8	2	5.54E-05	4	6.49E-02	4	4.83E-01	4	493	4320	8640	38900	6.87	4	4.34	2.17E+04	15			
BDE-52	485.8	25	161.7	2	5.07E-04	4	1.32E-01	4	1.87E+00	4	252	4320	8640	38900	6.65	4	4.12	1.32E+04	15			
BDE-49	485.8	25	161.7	2	4.31E-04	4	1.26E-01	4	1.66E+00	4	254	4320	8640	38900	6.66	4	4.12	1.32E+04	15			
BDE-47	485.8	25	84.0	4	3.13E-04	4	1.20E-01	4	1.27E+00	4	256	4320	8640	38900	6.66	4	5.96	9.17E+05	16			
BDE-66	485.8	25	161.7	2	2.08E-04	4	1.28E-01	4	7.88E-01	4	254	4320	8640	38900	6.44	4	5.94	8.76E+05	16			
BDE-77	485.8	25	98.0	2	2.27E-04	4	1.86E-01	4	5.92E-01	4	252	4320	8640	38900	5.95	4	4.12	1.32E+04	15			

Table A1. (Cont'd)

Chemical Name	Molar Mass (g/mol)	Data Temp. C°	Melting Point C°	Ref1	Vapor Pressure (Pa)	Ref2	Solubility in Water (g/m3)	Ref3	Henry's Law Constant (Pa*m3/mol)	Ref4	t1/2 in air (h)	t1/2 in water (h)	t1/2 in soil (h)	t1/2 in sediment (h)	LogKow	Ref5	log Koc	Koc (L/kg)	Ref6	Koc Pred.	Modified Koc	Notes
CFVP	359.6	25	-19.0	3	1.00E-04	3	1.24E+02	3	2.90E-04	3	4	1	4032	13000	3.82	3	3.11	1.29E+03	3	1.26E+03		No need to modify Koc
CFVP (EPI Suite)	359.6	25	85.9	2	1.26E-03	9	1.98E+01	12	5.23E-03	13	4	1440	2880	13000	4.15	14	3.10	1.26E+03	15			Intentional blank
Desethyl-CFVP	331.5	25	83.9	2	2.52E-06	9	7.39E+01	12	1.23E-05	13	6	1440	2880	13000	3.60	14	2.55	3.54E+02	15		3.54E+01	Anionic TPs from neutral parent compound
2,4-dichlorophenacyl chloride	223.5	25	78.0	2	1.10E-01	9	1.48E+02	12	1.92E-01	13	224	1440	2880	13000	3.22	14	2.42	2.60E+02	15		2.65E+02	Non-ionic TPs from experimentally known parent compound
1-(2,4-dichlorophenyl) ethane-1,2-diol	207.1	25	91.0	2	5.31E-04	9	1.26E+04	12	5.87E-04	13	19	900	1800	8100	1.72	14	1.00	1.00E+01	15		1.02E+01	Non-ionic TPs from experimentally known parent compound
PeCB	250.3	25	86.0	5	2.19E-01	5	6.58E-01	5	8.40E+01	5	4440	4320	8640	29	5.18	5	4.91	8.13E+04	3	3.71E+03		No need to modify Koc
PeCB (EPI Suite)	250.3	25	64.5	2	2.27E-01	9	1.49E+00	12	1.22E+02	13	4440	4320	8640	38900	5.22	14	3.57	3.71E+03	15			Intentional blank
1,2,3,5-TeCB	215.9	25	39.4	2	3.54E+00	9	6.32E+00	12	1.65E+02	13	1300	1440	2880	13000	4.57	14	3.35	2.22E+03	15		4.87E+04	Non-ionic TPs from experimentally known parent compound
1,2,4,5-TeCB	215.9	25	39.4	2	3.29E-01	9	6.32E+00	12	1.65E+02	13	3120	1440	2880	13000	4.57	14	3.35	2.22E+03	15		4.87E+04	Non-ionic TPs from experimentally known parent compound
1,3,5-TCB	181.5	25	16.4	2	1.29E+01	9	2.61E+01	12	2.22E+02	13	378	1440	2880	13000	3.93	14	3.12	1.33E+03	15		2.91E+04	Non-ionic TPs from experimentally known parent compound
1,2,4-TCB	181.5	25	16.4	2	2.44E+01	10	2.61E+01	12	2.22E+02	13	467	1440	2880	13000	3.93	14	3.13	1.36E+03	15		2.97E+04	Non-ionic TPs from experimentally known parent compound
1,3-DCB	147.0	25	-14.3	2	2.87E+02	6	1.04E+02	12	3.00E+02	13	357	900	1800	8100	3.28	14	2.57	3.75E+02	15		8.23E+03	Non-ionic TPs from experimentally known parent compound
Trichloromethane	119.4	25	-63.4	3	2.62E+04	3	8.20E+03	3	4.27E+02	3	1700	1700	5500	17000	1.97	3	1.46	2.88E+01	3	3.18E+01		No need to modify Koc
Trichloromethane (EPI Suite)	119.4	25	-78.9	2	2.51E+04	11	8.63E+03	12	3.26E+02	13	2450	900	1800	8100	1.52	14	1.50	3.18E+01	15			Intentional blank
Dichloromethane	84.9	25	-95.2	3	5.80E+04	3	1.32E+04	3	3.00E+02	3	1700	1700	5500	17000	1.25	3	1.00	1.00E+01	3			Experimental value no need modification
Methane	16.0	25	-182.6	6	6.21E+07	6	2.20E+01	6	6.67E+04	6	34100	360	720	3240	1.09	6	0.60	3.98E+00	15		3.61E+00	Non-ionic TPs from experimentally known parent compound
Aclonifen	264.7	25	81.5	7	1.60E-05	7	5.70E+00	12	1.70E-03	7	20	101	2808	343	4.04	7	3.39	2.45E+03	15			No need this part because all compounds including parent compound is estimated
Aclonifen (EPI Suite)	264.7	25	160.0	2	3.27E-04	9	5.70E+00	12	2.70E-04	13	20	1440	2880	13000	3.88	14	3.39	2.45E+03	15			
TP1Acl	250.7	25	162.4	2	2.89E-07	9	3.36E+02	12	2.21E-09	13	2	900	1800	8100	1.98	14	3.16	1.45E+03	15			
Bifenox	342.1	25	85.0	3	3.20E-04	3	3.50E-01	3	3.13E-01	3	245	1440	168	13000	4.48	3	4.36	2.29E+04	3	3.68E+03		No need to modify Koc
Bifenox (EPI Suite)	342.1	25	176.7	2	7.17E-05	9	1.14E+00	12	1.67E-04	13	245	1440	2880	13000	4.15	14	3.57	3.68E+03	15			Intentional blank
Methyl(2,4-dichlorophenoxy)anthranilate	312.2	25	158.5	2	2.42E-05	9	3.82E+00	12	1.49E-05	13	11	1440	2880	13000	4.77	14	3.06	1.14E+03	15		7.10E+03	Non-ionic TPs from experimentally known parent compound
HCBD	260.8	25	-21.0	8	3.20E+01	8	3.20E+00	8	1.04E+03	8	8530	4320	8640	38900	4.78	8	2.927	8.45E+02	15			No need this part because all compounds including parent compound is estimated
HCBD (EPI Suite)	260.8	25	-6.2	2	3.35E+01	11	4.86E+00	12	1.09E+03	13	8530	4320	8640	38900	4.72	14	2.927	8.45E+02	15			
PCBD	226.3	25	-21.3	2	1.02E+02	11	1.63E+01	12	1.52E+03	13	2200	1440	2880	13000	4.22	14	2.733	5.40E+02	15			
TeCBD	191.9	25	-36.7	2	1.22E+02	11	5.33E+01	12	2.11E+03	13	504	1440	2880	13000	3.73	14	2.538	3.45E+02	15			



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21. EPI Suite AOPWIN				

Colors with corresponding reference number given above.

🟨	20	🟦	19	🟧	3	🟩	18	🟨	1	⬜	17	🟫	16	🟦	21

END-TEXT REFERENCES FOR TABLE A1

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Table A2. FAVs for parent chemicals and their TPs.

Chemicals	Vapor pressure			Solubility in Water			Henry's Law Constant			$\log K_{OW}$		logKoa	Epsilon for VP, Sol, KH	Delta for VP, Sol, KH	Epsilon for Kow	Delta for Kow	Delta2 for Kow if logKow >4
	LDV (Pa)	Sa	FAV (Pa)	LDV (g/m³)	Sw	FAV (g/m3)	LDV (Pa·m³/mol)	Kaw	FAV (Pa.m3/mole)	LDV	FAV						
Atrazine	4.00E-05	1.61E-08	4.00E-05	30.0	1.39E-01	3.00E+01	2.88E-04	1.16E-07	2.88E-04	2.75	2.59E+00	9.08	0.00	0.00	0.49	0.16	
Atrazine (EPI Suite)	3.81E-03	1.54E-06	1.11E-03	45.0	2.09E-01	1.54E+02	4.53E-04	1.83E-07	1.55E-03	2.82	2.87E+00	9.58	-1.61	-0.54	-0.14	-0.05	
DEA	1.15E-02	4.64E-06	3.14E-03	282.5	1.51E+00	1.04E+03	1.55E-04	6.25E-08	5.68E-04	1.51	1.55E+00	8.71	-1.69	-0.56	-0.12	-0.04	
DIA	2.81E-02	1.13E-05	6.59E-03	537.0	3.09E+00	2.29E+03	1.17E-04	4.72E-08	4.99E-04	1.15	1.19E+00	8.47	-1.89	-0.63	-0.11	-0.04	
HA	1.13E-03	4.56E-07	1.18E-05	4.0	2.01E-02	3.81E+02	6.36E-08	2.57E-11	6.10E-06	2.09	2.13E+00	12.68	-5.95	-1.98	-0.12	-0.04	
Diuron	9.20E-05	3.71E-08	9.97E-05	4.00E+01	1.72E-01	3.69E+01	6.83E-04	2.76E-07	6.30E-04	2.78	3.16E+00	10.37	0.11	0.04	-1.14	-0.38	
Diuron (EPI Suite)	6.20E-04	2.50E-07	2.09E-04	1.02E+02	4.37E-01	3.03E+02	5.40E-05	2.18E-08	1.60E-04	2.67	2.72E+00	10.37	-1.42	-0.47	-0.15	-0.05	
DCPMU	0.00269	1.09E-06	6.23E-04	297.85	1.36E+00	1.29E+03	2.46E-05	9.92E-09	1.06E-04	2.46	2.66E+00	10.94	-1.91	-0.64	-0.60	-0.20	
MCPDMU	6.26E-03	2.53E-06	1.83E-03	427.3	2.15E+00	1.46E+03	7.29E-05	2.94E-08	2.49E-04	2.03	2.06E+00	9.53	-1.60	-0.53	-0.09	-0.03	
DCPU	4.34E-03	1.75E-06	7.41E-04	394.9	1.93E+00	2.31E+03	1.12E-05	4.52E-09	6.56E-05	2.00	2.25E+00	10.99	-2.30	-0.77	-0.76	-0.25	
DCA	4.09E-01	1.65E-04	5.29E-01	1350.9	8.34E+00	1.04E+03	1.06E-01	4.28E-05	8.20E-02	2.37	2.13E+00	5.91	0.33	0.11	0.71	0.24	
Alachlor	2.00E-03	8.07E-07	1.99E-03	240	8.90E-01	2.42E+02	2.20E-03	8.88E-07	2.22E-03	2.80	2.99E+00	9.31	-0.01	0.00	-0.58	-0.19	
Alachlor (EPI Suite)	2.73E-03	1.10E-06	3.03E-03	444.62	1.65E+00	4.01E+02	2.26E-03	9.12E-07	2.04E-03	3.37	3.60E+00	9.99	0.13	0.04	-0.69	-0.23	
Lactam	6.45E-04	2.60E-07	1.83E-03	1221.3	5.23E+00	4.30E+02	2.83E-03	1.14E-06	9.96E-04	2.60	2.64E+00	8.54	1.36	0.45	-0.12	-0.04	
Alachlor ESA	1.19E-09	4.80E-13	1.70E-08	1000000	3.17E+03	6.99E+04	1.10E-09	4.44E-13	7.69E-11	1.82	1.86E+00	14.18	3.47	1.16	-0.12	-0.04	
Alachlor OXA	3.10E-06	1.25E-09	1.43E-04	77093	3.07E+02	1.67E+03	1.00E-03	4.03E-07	2.16E-05	2.22	2.26E+00	8.61	5.00	1.67	-0.12	-0.04	
DEHP	1.91E-03	7.69E-07	1.91E-03	2.90E-02	7.41E-05	2.89E-02	2.59E+01	1.05E-02	2.59E+01	5.11	5.91E+00	10.53	0.00	0.00	-3.23	-1.08	-0.80
DEHP (EPI Suite)	2.70E-03	1.09E-06	3.06E-04	1.28E-03	3.27E-06	1.13E-02	1.20E+00	4.84E-04	1.06E+01	8.39	8.27E+00	12.56	-2.84	-0.95	0.50	0.17	0.12
MEHP	2.70E-03	1.09E-06	3.06E-04	1.28E-03	3.27E-06	1.13E-02	1.20E+00	4.84E-04	1.06E+01	8.39	8.27E+00	12.56	-2.84	-0.95	0.50	0.17	0.12
PA	1.02E-04	4.11E-08	7.43E-05	2.97E+04	1.79E+02	4.07E+04	2.21E-07	8.92E-11	3.03E-07	1.07	6.75E-01	9.82	-0.41	-0.14	1.19	0.40	
Dicofol	5.33E-05	2.15E-08	7.03E-06	8.00E-01	2.16E-03	6.07E+00	5.66E-05	2.28E-08	4.29E-04	3.54	3.20E+00	10.03	-2.64	-0.88	1.03	0.34	
Dicofol (EPI Suite)	9.18E-06	3.70E-09	1.58E-06	3.07E-01	8.30E-04	1.78E+00	5.67E-05	2.29E-08	3.29E-04	5.81	4.85E+00	10.03	-2.29	-0.76	3.88	1.29	0.96
Bis(4-chlorophenyl)methanone	8.52E-04	3.44E-07	1.35E-03	7.80E+00	3.11E-02	4.94E+00	1.08E-01	4.36E-05	6.84E-02	4.44	4.45E+00	8.80	0.60	0.20	-0.02	-0.01	-0.01
4-chlorophenyl phenyl methanone	1.48E-02	5.97E-06	1.70E-02	3.31E+01	1.53E-01	2.89E+01	1.46E-01	5.89E-05	1.27E-01	3.79	3.83E+00	8.02	0.18	0.06	-0.12	-0.04	
Diphenylmethanone	1.16E-01	4.68E-05	1.26E-01	1.37E+02	7.52E-01	1.26E+02	1.97E-01	7.95E-05	1.82E-01	3.15	3.20E+00	7.28	0.11	0.04	-0.15	-0.05	
DDT	2.00E-05	8.07E-09	2.01E-05	5.50E-03	1.55E-05	5.47E-03	1.31E+00	5.28E-04	1.30E+00	6.19	6.13E+00	9.81	0.01	0.00	0.24	0.08	0.06
DDT (EPI Suite)	3.21E-01	1.29E-04	1.16E-02	3.43E-03	9.66E-06	9.51E-02	1.55E+00	6.25E-04	4.31E+01	6.79	6.69E+00	10.38	-4.33	-1.44	0.41	0.14	0.10
DDE	8.66E-04	3.49E-07	7.34E-04	4.00E-02	1.26E-04	4.72E-02	4.20E+00	1.69E-03	4.95E+00	5.70	5.90E+00	9.69	-0.21	-0.07	-0.80	-0.27	-0.20
DDD	1.30E-04	5.24E-08	1.21E-04	5.00E-02	1.56E-04	5.37E-02	6.70E-01	2.70E-04	7.20E-01	5.50	5.67E+00	10.10	-0.09	-0.03	-0.69	-0.23	-0.17
DDDNU	1.65E-02	6.66E-06	1.39E-02	3.59E-01	1.44E-03	4.25E-01	6.88E+00	2.78E-03	8.15E+00	5.15	5.10E+00	7.71	-0.22	-0.07	0.22	0.07	0.05
Trifluralin	2.60E-02	1.05E-05	1.60E-02	5.00E-01	1.49E-03	8.15E-01	4.03E+00	1.62E-03	6.56E+00	5.34	5.17E+00	7.72	-0.64	-0.21	0.70	0.23	0.17
Trifluralin (EPI Suite)	1.80E-03	7.26E-07	2.25E-03	5.50E-02	1.64E-04	4.39E-02	2.15E+01	8.67E-03	1.72E+01	5.31	5.33E+00	7.72	0.29	0.10	-0.07	-0.02	-0.02
TR-4	4.31E-04	1.74E-07	1.01E-04	2.34E-01	7.68E-04	1.00E+00	7.15E-03	2.88E-06	3.06E-02	4.58	4.57E+00	10.12	-1.89	-0.63	0.02	0.01	0.01
TR-7	1.18E-03	4.76E-07	6.64E-05	1.97E+00	7.17E-03	3.51E+01	2.93E-05	1.18E-08	5.21E-04	3.26	3.30E+00	11.19	-3.75	-1.25	-0.12	-0.04	
TR-9	1.87E-02	7.54E-06	6.86E-04	8.46E+02	4.43E+00	2.30E+04	2.09E-07	8.43E-11	5.69E-06	0.20	2.38E-01	10.27	-4.31	-1.44	-0.11	-0.04	

Table A2. (Cont'd)

Chemicals	Vapor pressure			Solubility in Water			Henry's Law Constant			$\log K_{OW}$		logKoa	Epsilon for VP, Sol, KH	Delta for VP, Sol, KH	Epsilon for Kow	Delta for Kow	Delta2 for Kow if logKow >4
	LDV (Pa)	Sa	FAV (Pa)	LDV (g/m³)	Sw	FAV (g/m3)	LDV (Pa·m³/mol)	Kaw	FAV (Pa.m3/mole)	LDV	FAV						
Chlorpyrifos	2.27E-03	9.16E-07	1.72E-03	7.30E-01	2.08E-03	9.65E-01	4.72E-01	1.90E-04	6.24E-01	4.92	4.91E+00	8.75	-0.36	-0.12	0.03	0.01	0.01
Chlorpyrifos (EPI Suite)	2.73E-03	1.10E-06	3.91E-03	1.10E+01	3.14E-02	7.68E+00	2.56E-01	1.03E-04	1.79E-01	5.11	5.01E+00	8.88	0.47	0.16	0.42	0.14	0.10
Chlorpyrifos oxon	8.87E-04	3.58E-07	1.51E-03	2.62E+03	7.84E+00	1.55E+03	5.53E-04	2.23E-07	3.26E-04	2.89	2.93E+00	9.54	0.69	0.23	-0.12	-0.04	
TCP	1.38E-01	5.57E-05	2.84E-02	1.25E+02	6.30E-01	6.08E+02	1.91E-03	7.71E-07	9.28E-03	3.01	3.12E+00	9.32	-2.06	-0.69	-0.32	-0.11	
BDE-153	7.58E-06	3.06E-09	8.41E-06	1.95E-02	3.03E-05	1.76E-02	3.42E-01	1.38E-04	3.08E-01	7.13	7.11E+00	11.82	0.14	0.05	0.09	0.03	0.02
BDE-153 (EPI Suite)	3.83E-07	1.55E-10	2.82E-07	2.07E-03	3.22E-06	2.81E-03	4.77E-02	1.92E-05	6.47E-02	8.55	8.20E+00	13.27	-0.40	-0.13	1.41	0.47	0.35
BDE-101	3.25E-06	1.31E-09	2.89E-06	1.07E-02	1.89E-05	1.21E-02	1.20E-01	4.84E-05	1.35E-01	7.66	7.39E+00	11.98	-0.16	-0.05	1.10	0.37	0.27
BDE-99	4.57E-05	1.84E-08	3.78E-05	2.75E-02	4.87E-05	3.33E-02	5.30E-01	2.14E-04	6.41E-01	6.61	6.68E+00	11.31	-0.25	-0.08	-0.30	-0.10	-0.07
BDE-118	3.25E-06	1.31E-09	2.89E-06	1.07E-02	1.89E-05	1.21E-02	1.20E-01	4.84E-05	1.35E-01	7.66	7.39E+00	11.98	-0.16	-0.05	1.10	0.37	0.27
BDE-52	3.21E-05	1.29E-08	3.26E-05	5.42E-02	1.12E-04	5.34E-02	3.01E-01	1.21E-04	2.96E-01	6.77	6.58E+00	10.69	0.02	0.01	0.79	0.26	0.19
BDE-49	3.21E-05	1.29E-08	3.26E-05	5.42E-02	1.12E-04	5.34E-02	3.01E-01	1.21E-04	2.96E-01	6.77	6.58E+00	10.69	0.02	0.01	0.79	0.26	0.19
BDE-47	2.66E-04	1.07E-07	2.00E-04	4.96E-02	1.02E-04	6.60E-02	1.11E+00	4.47E-04	1.47E+00	6.11	6.24E+00	10.53	-0.37	-0.12	-0.51	-0.17	-0.13
BDE-66	1.22E-04	4.92E-08	5.50E-05	1.80E-02	3.71E-05	4.00E-02	3.01E-01	1.21E-04	6.68E-01	6.77	6.61E+00	10.82	-1.04	-0.35	0.66	0.22	0.16
BDE-77	1.20E-04	4.84E-08	3.77E-05	6.00E-03	1.24E-05	1.91E-02	3.01E-01	1.21E-04	9.58E-01	7.61	7.18E+00	10.87	-1.51	-0.50	1.74	0.58	0.43
CFVP	1.00E-04	4.03E-08	1.00E-04	1.24E+02	3.45E-01	1.24E+02	2.90E-04	1.17E-07	2.90E-04	3.82	3.52E+00	9.74	0.00	0.00	0.90	0.30	
Chlorfenvinphos (EPI Suite)	1.26E-03	5.08E-07	7.70E-04	1.98E+01	5.50E-02	3.24E+01	5.23E-03	2.11E-06	8.56E-03	4.15	4.16E+00	9.74	-0.64	-0.21	-0.04	-0.01	-0.01
Desethyl-chlorfenvinphos	2.52E-06	1.02E-09	2.59E-06	7.39E+01	2.23E-01	7.18E+01	1.23E-05	4.96E-09	1.20E-05	3.60	3.64E+00	11.90	0.04	0.01	-0.11	-0.04	
2,4-dichlorophenacyl chloride	1.10E-01	4.44E-05	1.16E-01	1.48E+02	6.64E-01	1.41E+02	1.92E-01	7.75E-05	1.83E-01	3.22	3.26E+00	7.33	0.06	0.02	-0.12	-0.04	
1-(2,4-dichlorophenyl) ethane-1,2-diol	5.31E-04	2.14E-07	2.16E-03	1.26E+04	6.07E+01	3.09E+03	5.87E-04	2.37E-07	1.44E-04	1.72	1.76E+00	8.35	1.83	0.61	-0.12	-0.04	
PeCB	2.19E-01	8.83E-05	2.19E-01	6.58E-01	2.63E-03	6.56E-01	8.40E+01	3.39E-02	8.37E+01	5.18	5.18E+00	6.90	0.00	0.00	-0.02	-0.01	0.00
PeCB (EPI Suite)	2.27E-01	9.16E-05	3.34E-01	1.49E+00	5.95E-03	1.01E+00	1.22E+02	4.92E-02	8.28E+01	5.22	5.21E+00	6.72	0.50	0.17	0.05	0.02	0.01
1,2,3,5-TeCB	3.54E+00	1.43E-03	3.93E+00	6.32E+00	2.93E-02	5.70E+00	1.65E+02	6.66E-02	1.49E+02	4.57	4.57E+00	5.75	0.13	0.04	0.02	0.01	0.00
1,2,4,5-TeCB	3.29E-01	1.33E-04	8.06E-01	6.32E+00	2.93E-02	2.58E+00	1.65E+02	6.66E-02	6.74E+01	4.57	4.63E+00	6.03	1.17	0.39	-0.26	-0.09	-0.06
1,3,5-TCB	1.29E+01	5.20E-03	1.75E+01	2.61E+01	1.44E-01	1.93E+01	2.22E+02	8.96E-02	1.64E+02	3.93	4.08E+00	5.30	0.39	0.13	-0.44	-0.15	
1,2,4-TCB	2.44E+01	9.84E-03	2.67E+01	2.61E+01	1.44E-01	2.39E+01	2.22E+02	8.96E-02	2.03E+02	3.93	4.06E+00	5.26	0.12	0.04	-0.40	-0.13	
1,3-DCB	2.87E+02	1.16E-01	2.60E+02	1.04E+02	7.08E-01	1.15E+02	3.00E+02	1.21E-01	3.32E+02	3.28	3.42E+00	4.50	-0.13	-0.04	-0.42	-0.14	
Trichloromethane	2.62E+04	1.06E+01	2.72E+04	8.20E+03	6.87E+01	7.90E+03	4.27E+02	1.72E-01	4.11E+02	1.97	2.03E+00	2.80	0.05	0.02	-0.18	-0.06	
Trichloromethane (EPI Suite)	2.51E+04	1.01E+01	2.46E+04	8.63E+03	7.23E+01	8.81E+03	3.26E+02	1.32E-01	3.33E+02	1.52	1.69E+00	2.79	-0.03	-0.01	-0.51	-0.17	
Dichloromethane	5.80E+04	2.34E+01	5.39E+04	1.32E+04	1.55E+02	1.42E+04	3.00E+02	1.21E-01	3.23E+02	1.25	1.32E+00	2.27	-0.09	-0.03	-0.22	-0.07	
Methane	6.21E+07	2.51E+04	7.07E+06	2.20E+01	1.37E+00	1.93E+02	6.67E+04	2.69E+01	5.86E+05	1.09	1.13E+00	-0.34	-2.83	-0.94	-0.12	-0.04	
Aclonifen	1.60E-05	6.45E-09	2.11E-05	5.70E+00	2.15E-02	4.33E+00	1.70E-03	6.86E-07	1.29E-03	4.04	4.08E+00	10.21	0.36	0.12	-0.17	-0.06	-0.04
Aclonifen (EPI Suite)	3.27E-04	1.32E-07	8.54E-05	5.70E+00	2.15E-02	2.18E+01	2.70E-04	1.09E-07	1.03E-03	3.88	3.71E+00	10.21	-1.75	-0.58	0.52	0.17	
TP1Acl	2.89E-07	1.17E-10	6.28E-08	3.36E+02	1.34E+00	1.55E+03	2.21E-09	8.92E-13	1.02E-08	1.98	2.02E+00	14.03	-1.99	-0.66	-0.12	-0.04	
Bifenox	3.20E-04	1.29E-07	3.20E-04	3.50E-01	1.02E-03	3.50E-01	3.13E-01	1.26E-04	3.13E-01	4.48	4.84E+00	9.84	0.00	0.00	-1.47	-0.49	-0.36
Bifenox (EPI Suite)	7.17E-05	2.89E-08	1.42E-05	1.14E+00	3.35E-03	5.77E+00	1.67E-04	6.74E-08	8.42E-04	4.15	3.81E+00	9.84	-2.11	-0.70	1.36	0.45	0.34
Methyl(2,4-dichlorophenoxy)anthranilate	2.42E-05	9.76E-09	4.75E-06	3.82E+00	1.22E-02	1.95E+01	1.49E-05	6.01E-09	7.60E-05	4.77	4.75E+00	12.99	-2.12	-0.71	0.09	0.03	0.02
HCBD	3.20E+01	1.29E-02	2.36E+01	3.20E+00	1.23E-02	4.34E+00	1.04E+03	4.21E-01	1.42E+03	4.78	4.76E+00	5.16	-0.40	-0.13	0.09	0.03	0.02
HCBD (EPI Suite)	3.35E+01	1.35E-02	2.84E+01	4.86E+00	1.86E-02	5.74E+00	1.09E+03	4.40E-01	1.29E+03	4.72	4.72E+00	5.16	-0.22	-0.07	-0.01	0.00	0.00
PCBD	1.02E+02	4.11E-02	1.04E+02	1.63E+01	7.20E-02	1.59E+01	1.52E+03	6.13E-01	1.48E+03	4.22	4.25E+00	4.43	0.03	0.01	-0.10	-0.03	-0.03
TeCBD	1.22E+02	4.92E-02	2.06E+02	5.33E+01	2.78E-01	3.16E+01	2.11E+03	8.51E-01	1.25E+03	3.73	3.77E+00	3.79	0.68	0.23	-0.11	-0.04	

🟧	Mackay et al., 2006	🟩	EPI Suite, KOAWIN	🟨	EPI Suite Experimental Database

END-TEXT REFERENCES FOR TABLE A2

Mackay, D., Shiu, W.Y., Shiu, W.Y., Lee, S. (2006). Handbook of Physical Chemical Properties and Environmental Fate for Organic Chemicals. Boca Raton: CRC Press, https://doi.org/10.1201/9781420044393