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Modelación matemática de la contaminación de suelos y aguas subterráneas por pesticidas orgánicos: aplicación al acuífero de la plana de Valencia

Memoria

Trabajo final de grado

Titulación: Ingeniería de Obras Públicas

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a. Summary of the thesis

After increasing application of pesticides in the last century, more and more concerns about uncontrolled pesticide application appeared. Until today neither their long-time effects on human and plant health are completely clear nor are the processes of transport and fate of pesticide in the environment fully understood. As pesticide application plays a decisive role in topics like food security, human health, sustainability in alimentation, anthropogenic environmental impacts and water quality in general, regulations and control of pesticide use is important. To allow competent and reasonable decision-making about pesticide management, models of the fate and transport of pesticides are necessary.

This thesis is a description of the state-of-art of available models for fate and transport of pesticide, concentrating on soil and groundwater as contaminated media. How these models, on the example of PESTAN, work and how adequate and realistic the results are, is being investigated. This paper also discusses the complex processes determining fate of pesticides in nature, like advection, dispersion, biodegradation, mass transfer and reaction transformations. Furthermore it describes the equations on which the simulations of the model are based, gives an overview on the output data and includes an estimation of the sensitivity of the model to variations in input data. For the application, data from the plain of Valencia is used. Also there is an overview of available models for pesticide management included.

Additionally a short summary of different types of pesticides is given, differencing due to their molecular structure between organochlorines, organophosphates, carbamates, triazines, plant insecticides and fumigants. There is a huge variety of chemicals available, increasing every year. For a responsible application, prior registration and profound tests of these chemicals are necessary.

For testing the functionality of PESTAN as modeling program finally the application of the example data based on real circumstances in the plain of Valencia is analysed. The different types of output files are explained and shown. In addition variations due to apparently rather slightly changes in soil type (sandy loam to loamy sand) are applied and the differences in the results are analyzed. Also sensitivity and variations in the output data due to increasing and decreasing amount of pesticide discharged are tested.

Keywords: Organic, Pesticides, Modelling, Soil, Groundwater

b. Resumen del trabajo

Despues de un aumento en la aplicación de pesticidas en el último siglo, existen cada vez más dudas acerca de la aplicación incontrolada de pesticidas. Hasta hoy, ni sus efectos a largo plazo sobre la salud humana y vegetal son completamente conocidos ni lo son los procesos de transporte de los plaguicidas en el medio ambiente. Como la aplicación de plaguicidas desempeña un papel decisivo en temas como la seguridad alimentaria, la salud humana, la sostenibilidad de la alimentación, los impactos ambientales antropogénicos y la calidad del agua en general; la regulación y el control del uso de plaguicidas es importante. Para permitir una competente y razonable toma de decisiones sobre el manejo de plaguicidas, son necesarios modelos del comportamiento y del transporte de los plaguicidas.

Esta tesis es una descripción del nivel de la técnica de los modelos disponibles para el destino y el transporte de los plaguicidas, centrándose en el suelo y las aguas subterráneas como medios contaminados. Se ha investigado cómo estos modelos, por ejemplo el PESTAN, trabajan y cómo de adecuados y realistas son los resultados. Este documento también analiza los procesos complejos que determinan el comportamiento de los plaguicidas en la naturaleza como advección, dispersión, biodegradación, transferencia de masa y reacciónes de transformaciones. Además están descritas las ecuaciones en que se basan las simulaciones, ofreciéndose una visión general de los datos del output incluyendo una estimación de la sensibilidad del modelo a las variaciones en los datos de input. Para la aplicación se usan datos de la plana de Valencia. También se incluye un resumen de los modelos disponibles para la gestión de los plaguicidas.

Además se da una breve visión general de los diferentes tipos de pesticidas, diferenciada por su estructura molecular entre organoclorados, organofosfatos, carbamatos, triazinas, insecticidas vegetales y fumigantes. Existe una gran variedad de productos químicos disponibles que pueden estár usado como pesticidas, y aún este número aumenta cada año. Para una aplicación responsable es necesario el registro y pruebas profundas de estos productos.

Para probar la funcionalidad de PESTAN como programa de modelación por último se analiza la aplicación de los datos de ejemplo en base a las circunstancias reales en la plana de Valencia. Los diferentes tipos de output son explicados y mostrados. Además se aplican y se analizan las variaciones debido a los cambios ligeros aparentes en el tipo de suelo (arena arcillosa a franco arenoso) en los resultados. También se estudian la sensibilidad y variaciones en los datos de salida debido al aumento y la disminución de cantidad de pesticida descargada.

Palabras claves: Organic, pesticidas, modelación, suelo, agua subterránea

c. Resum del treball

Després d'un augment en l'aplicació de pesticides en l'últim segle, existeixen cada volta més dubtes al voltant de l'aplicació incontrolada de pesticides. Fins a l'actualitat, ni els seus efectes a llarg termini sobre la salut humana i vegetal son completament coneguts ni ho son els processos de transport de plaguicides al medi ambient. Com l'aplicació de plaguicides juga un papar decisiu en temes com la seguretat alimentaria, la salut humana, la sostenibilitat de la alimentació, els impactes ambientals antropogènics i la qualitat de l'aigua en general; la regulació i el control de l'ús d'aquestos plaguicides es important. Per a permetre una competent i raonable presa de decisions sobre l'ús de plaguicides, son necessaris models de comportament i de transport de plaguicides.

Esta tesis es una descripció del nivell de la tècnica dels models disponibles per a destí i el transport de plaguicides, centrant-se en el sol i les aigües subterrànies com a medis contaminats. S'ha investigat com estos models, per exemple el PESTAN, treballen i com d'adequats i realistes son els resultats. Aquest document també analitza els processos complexos que determinen el comportament dels plaguicides a la natura com advecció, dispersió, biodegradació, transferència de massa i reaccions de transformació. A més estan descrites les equacions en que es basen les simulacions oferint una visió general de les dades outpur incloent un anàlisis de sensibilitat del model a les variacions de les dades input. Per a la aplicació s'utilitzen dades de la plana de València. També s'inclou un resum dels models disponibles per a la gestió de plaguicides.

A més es dona una breu visió general dels diferents tipus de pesticides, diferenciats per la seua estructura molecular entre organoclorats, organofosfats, carbamats, triazines, insecticides vegetals i fumigants. Existeix una gran varietat de productes químics disponibles que poen estar utilitzant com a pesticides, i encara el número augmenta any rere any. Per a una aplicació responsable es necessari un registre i proves detallades d'aquestos productes.

Per a provar la funcionalitat de PESTAN com a programa de modelació per últim s'analitza l'aplicació e dades de exemple en base a circumstàncies reals de la plana de Valencia. Els diferents tipus de outputs son explicats i mostrats. A més s'apliquen i analitzen les variacions degudes a lleugers canvis aparents en el tipus de sol (arena argilosa a franc arenosa) en els resultats. També s'estudien la sensibilitat i variació de les dades d'eixida degut al augment i la disminució de pesticida descarregada.

Paraules claus: Orgànic, pesticides, modelació, sòl, aigua subterrània,

Bachelorthesis

MATHEMATICAL MODELING OF GROUNDWATER AND SOIL CONTAMINATION BY ORGANIC PESTICIDES: Application to aquifer of the plain of Valencia

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MATHEMATICAL MODELING OF GROUNDWATER AND SOIL CONTAMINATION BY ORGANIC PESTICIDES:

Application to aquifer of the plain of Valencia

1. Introduction and objectives of the study

a. Introduction to the topics in discussion

Since World War II the application of pesticides has increased all over the world, in developing as well as in industrial countries. Still, not before the Seventies and Eighties the wide environmental impact of pesticides was recognized. More and more concerned opinions about the limitless use of pesticides appeared. Even though investigations and protection measurements about these chemicals were set, still there is a lot of knowledge missing about their fate and transport in subsurface, air and water as well as about their long-time impacts on human and plant health.

Today pesticide use and especially their impact on human health due to residues on our daily food are widely discussed. They and a lot of directly related topics like food security, human health, sustainability in alimentation, anthropogenic environmental impacts and water quality in general play a decisive role in many actual regulations of governments and organizations worldwide, for example in the Transatlantic Trade and Investment Partnership (TTIP) or in the EU Water Framework Directive. Also the public gets more sensible to this controversially discussed topic. On the one hand pesticide use is important for food security, especially in a century with rapidly growing human population. On the other hand impacts on human health cannot be determined securely and hazardous environmental effects of many pesticides are proven.

To be able to manage pesticide use, make responsible decisions about their application and be able to set effective and adequate regulations, modeling of the fate of pesticides is important. To do so, various processes in the environment have to be taken into account. They result in a complex system of reactions and transport mechanisms affecting the pesticide and the media through which it passes. To calculate these, numerous equations have been developed, challenged to describe natural processes as simple as possible without losing accuracy and reality.

For the simulation of the results of all these equation describing fate and transport of pesticides, different models were introduced. They vary concerning amount and quality of input data they need, preciseness and complexity of calculations they use as well as in type of output data - different numeric results as well as different modes of illustration are available.

b. Objectives of this thesis

The main objective of this thesis is to describe the state-of-art of available models for fate and transport of pesticide, concentrating on soil and groundwater as contaminated media. The question is how these models, on the example of PESTAN, work and how adequate and realistic the results are. This paper discusses the processes included in the calculations of the PESTAN model, describes the equations on which the simulations are based, gives an overview on the output data and includes an estimation of the sensitivity of the model to variations in input data.

To illustrate the application of the PESTAN model, an example of the plain of Valencia is used. This example is based on real data due to Ilarri, 2010; the pesticide applied is Chlorpyrifos.

In this thesis also the importance to control and regulate pesticide use is explained. Therefore it includes some information about water scarcity as well as the necessity to handle and treat our soils with care. They are the most important source for food and are affected highly by pesticide application. Concerning water especially groundwater is taken into account, as it is a main water resource in many parts of the world and contamination due to pesticides is difficult to estimate.

Additionally a short overview to the different types of pesticides is given. There is a huge variety of chemicals available and every year new ones are developed. They all should be tested and registered before applied as pesticide to control their impact and assure their responsible application.

To be able to understand the transport and fate of pesticides in the environment, knowledge about processes by which they are determined is necessary. This paper also includes a description of the main processes and reactions that appear in nature due to pesticide contamination.

Also an attempt to summarize and describe available models for the estimation of pesticide contamination is made. These include models for the estimation of pesticide contamination in soil and groundwater, calculations of risk indicators as well as programs for modeling fate of pesticides in the surface water.

2. Groundwater and soil contamination sources

a. General description of the problem

i. Water use for agriculture and food production

On average seven thousand five hundred liters of water are used by each American per day, mainly for food. Actually for the irrigation of one calorie only one liter of water is necessary. Due to inefficient water use this amount can exceed up to hundred liters per food calorie. Indeed this misuse is even more significant in developing countries, where water used for irrigation requires up to ninety percent of the total water withdrawal. But also globally seen, with seventy percent of the whole water withdrawal, agriculture is the one main user of water. And this number is about to increase. As estimated in the year 2050 there will be a need of food production increased about sixty percent. In developing countries it is even likely that hundred percent more will be demanded.

Growing economy and individual wealth lead to a change in diets: In the past human nutrition was based on starch; this is being more and more replaced by a diet dominated by meat and dairy. Production of this type of food is far more water intensive, thus water demand increases. For example for the production of one kilo rice three thousand liters of water are needed, whilst producing one kilo of beef requires fifth teen thousand liters. In the past thirty years this shift in diet affected water consumption highly and unfortunately trends indicate an increase at least until the middle of our century.

For the world's freshwater resources the present increasing amount of demand in agriculture and crop production is not sustainable. Problems caused by this inefficient use of water are reduction of river flows, degradation of wildlife habitats and depletion of aquifers. Additionally it can also be seen as the main factor for salinization of twenty percent of the global irrigated land area. As a necessary consequence efficiency in the use of water should be increased. This may lead to a reduction of water losses and growing crop productivity.

Conversely an increase in intensive agriculture will lead to more water pollution. As seen in countries of high income one possibility to reduce water pollution is a combination of incentives, including more stringent regulation, enforcement and subsidies that are well targeted. (UN Water, 2015)

On the whole one of the main problems we will have to face in the 21st century is the rapid decline in availability and quality of freshwater. What makes it more serious is that due to population growth and rising per capita withdrawal these changes go along with an increasing demand for this valuable resource. (Morris et al., 2003, p.11)

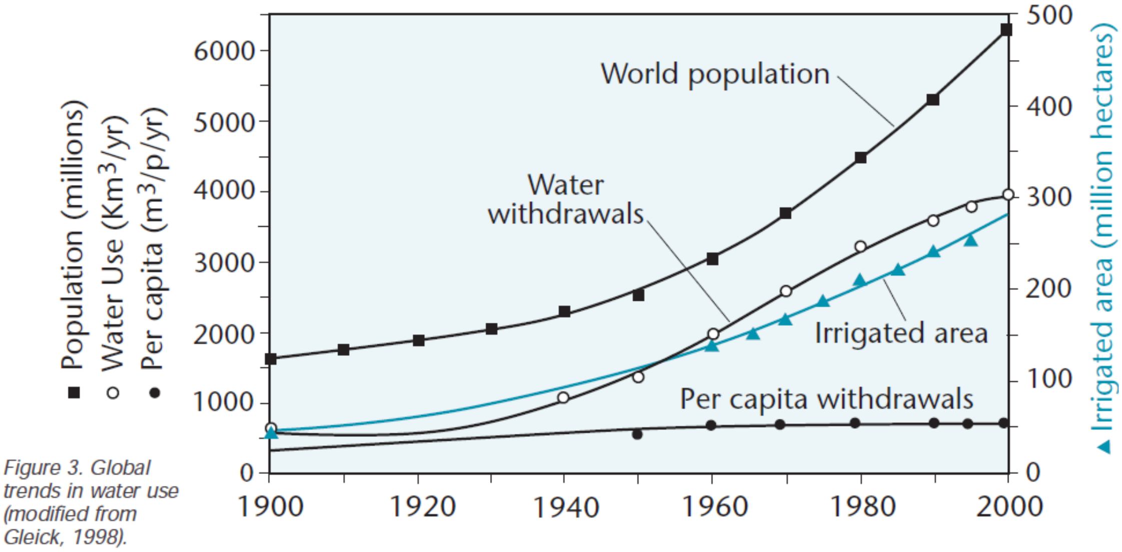


figure 1: Developments concerning water resource (Morris et al., 2003, p.5)

As seen in the graph above (*figure 1*), the world's population increased from a little more than one thousand five hundred million people in 1900 to more than six billion people in the year 2000. More or less at the same proportional extent water use and irrigated area expanded. In this figure it is not seen very dramatically but due to increasing water supply, sanitation and improvements of the living standards in the developing world also the per capita use has grown significantly. (Morris et al., 2003, pp.5-7)

In July 2010 the United Nations General Assembly declared the human right to water and sanitation. This should encourage the international community and governments to provide financial and technical resources to satisfy the basic human need for water and sanitation all over the world, especially in developing countries. (United Nations General Assembly, 2010)

Furthermore in November 2002 the Committee on Economic, Social and Cultural Rights stated:

> "The human right to water is indispensable for leading a life in human dignity. It is a prerequisite for the realization of other human rights". (United Nations Economic and Social Council, 2002)

ii. Importance of Groundwater

To fulfill the goals stated above groundwater is essential. About ninety five percent of the planets freshwater resources exist as groundwater (not counting the water of the polar ice caps). Worldwide approximately two billion people depend on aquifers as supply for their drinking water and fourty percent of the world's food is produced in agricultural areas which rely mostly on groundwater.

There are many reasons why **groundwater** is such a **fundamental water resource**:

It is stored in **enormous natural underground reservoirs** with huge capacity (e.g. Ogalalla aquifer, central USA: 500 km^3 of groundwater in four decades). They are in particular important in dry period, when correspondent superficial water resources such as rivers and lakes cannot satisfy the water demand.

Groundwater is relatively **easy to extract**: It requires little capital outlay and thanks to its relative ubiquity wells can often be constructed near where the water supply is needed. The construction, operation and control of the supply can be done more or less easily by an individual.

A **protective soil layer**, depending on its own grade of pollution generates a **natural filtration** of the water passing through; in consequence untreated groundwater is generally less contaminated than unprocessed water at the surface. As this layer makes the resources more or less invisible the awareness of groundwater as important and to-be-protected water resource is relatively recent. It also means that contamination often cannot be tracked for a long period of time and these areas are very difficult to remediate.

As a result of these characteristics the extent of the use of groundwater tends to be underestimated. The following data should give an impression of the importance of groundwater as resource for the human race.

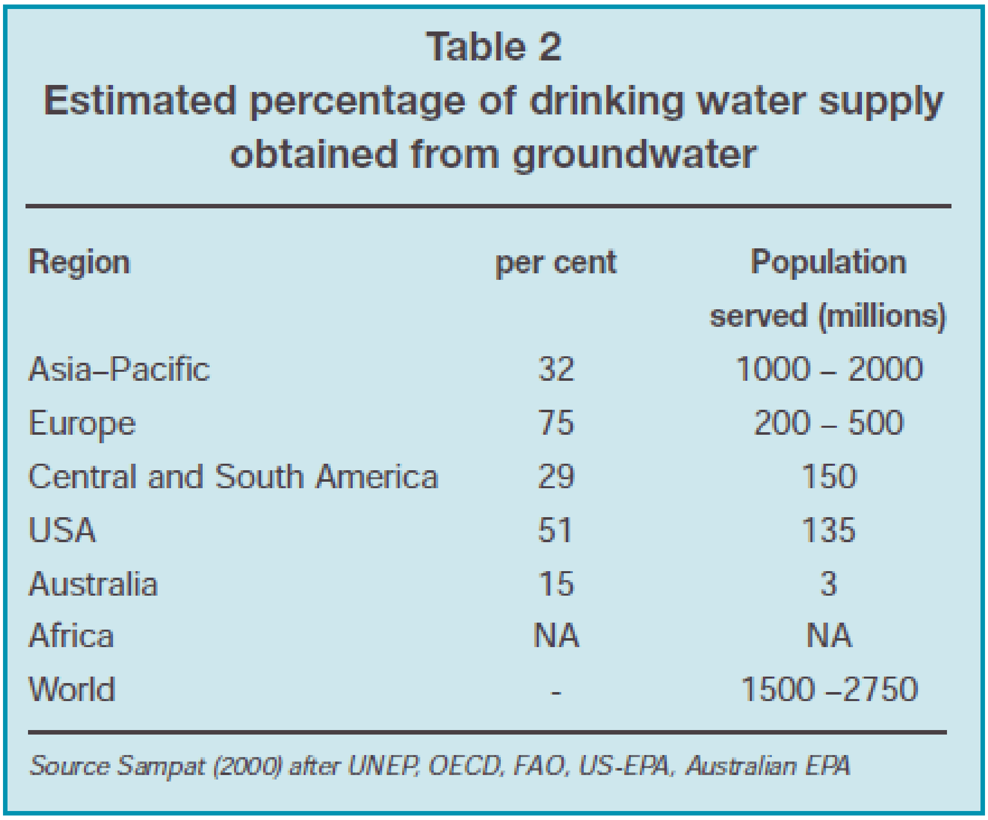


Table 2
Estimated percentage of drinking water supply obtained from groundwater

Region	per cent	Population served (millions)
Asia–Pacific	32	1000 – 2000
Europe	75	200 – 500
Central and South America	29	150
USA	51	135
Australia	15	3
Africa	NA	NA
World	-	1500 –2750

Source Sampat (2000) after UNEP, OECD, FAO, US-EPA, Australian EPA

figure 2: Groundwater as drinking water supply (Morris et al, 2003, p.3)

Figure 2 shows the dependency and importance of groundwater as a resource for drinking water all over the world. In Europe for instance about seventy five percent of the population use groundwater to satisfy their demand of drinking water. In the Asian-pacific area one to two billion people are served by groundwater as their drinking supply. This makes it the mayor resource for potable water for about thirty two percent of the population there. Worldwide it is estimated that one thousand five hundred to two thousand seven hundred and fifty millions of people obtain their drinking water from groundwater resources.

The data in *figure 3* illustrates that in the year 2000 half of the cities classified as megacities (more than 10 million inhabitants) like Mexican City, Buenos Aires, Calcutta, Cairo or Beijing made use of the local groundwater as a significant part of their water supply.

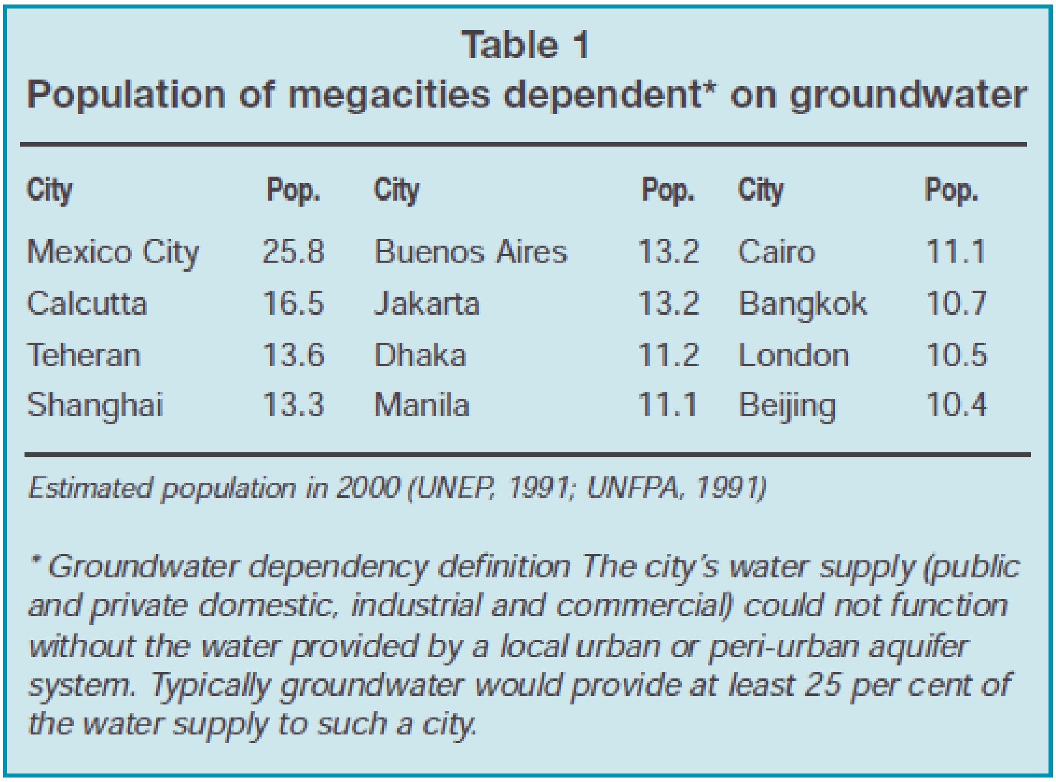


Table 1
Population of megacities dependent* on groundwater

City	Pop.	City	Pop.	City	Pop.
Mexico City	25.8	Buenos Aires	13.2	Cairo	11.1
Calcutta	16.5	Jakarta	13.2	Bangkok	10.7
Teheran	13.6	Dhaka	11.2	London	10.5
Shanghai	13.3	Manila	11.1	Beijing	10.4

Estimated population in 2000 (UNEP, 1991; UNFPA, 1991)

** Groundwater dependency definition The city's water supply (public and private domestic, industrial and commercial) could not function without the water provided by a local urban or peri-urban aquifer system. Typically groundwater would provide at least 25 per cent of the water supply to such a city.*

figure 3: Megacities and their groundwater dependency (Morris et al., 2003, p.2)

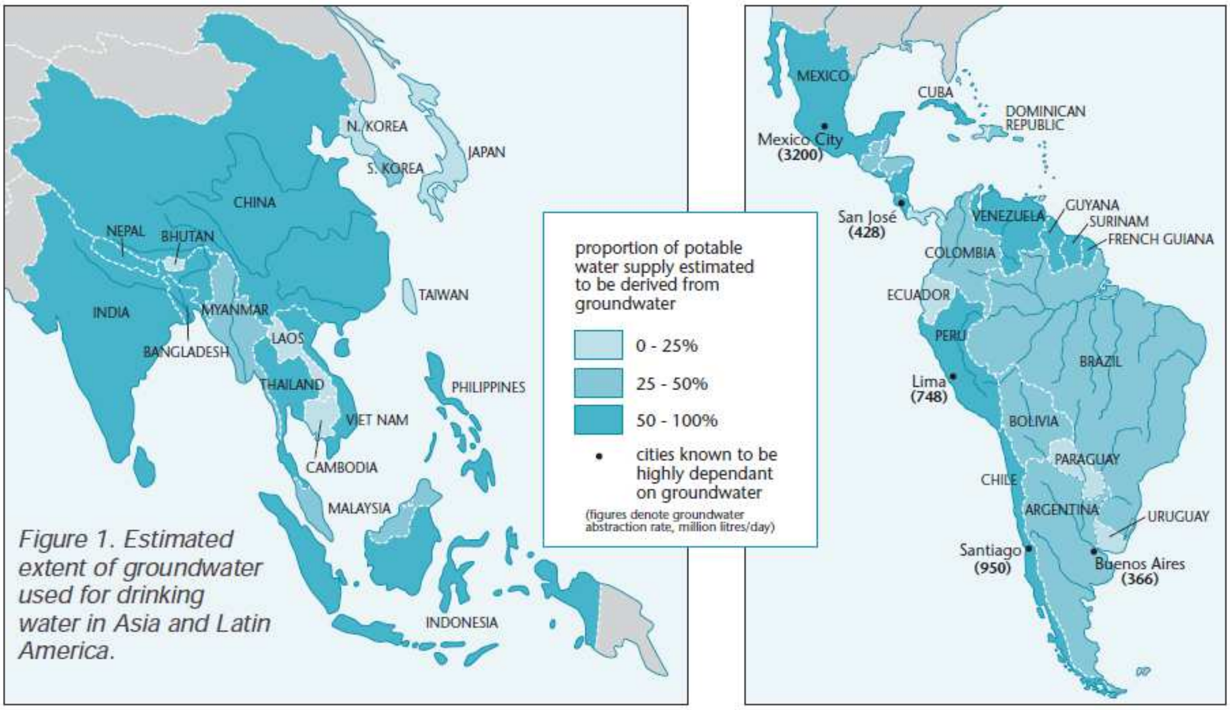


figure 4: Role of groundwater in Asia and Latin America (Morris et al., 2003, p.2)

In China two thirds of the water supply for its more than five hundred cities are extracted from aquifers. How highly dependent Asia and Central and South America are on groundwater also underlines *figure 4* on the previous.

In countries like China, India, Nepal and Thailand in Asia it is estimated that more than fifty percent of the potable water supply derives from groundwater. These numbers can also be applied on countries in Latin America like Peru, Venezuela and Mexico. In these areas in addition some cities like Lima, Mexico City, Buenos Aires and Santiago are known to be especially dependent on groundwater.

The use of groundwater for water supply in rural areas and small towns on its part is difficult to estimate, as the data of private domestic water supply is unreliable and equivocal and some towns use a mixture of surface and groundwater. Nevertheless it can be said that importance of groundwater in these areas is even higher. In China for example it is estimated that nearly one hundred and sixty million people meet their water demands from groundwater from the Huang-Huai-Hai aquifer. In the rural areas of the USA more than ninety five percent of the population rely on groundwater to supply their drinking water request. (Morris et al., 2003, pp.1-8)

iii. Soil

As already mentioned, as it filters water passing through it, the protective soil layer and its grade of contamination is a very important factor to assure an adequate quality of groundwater. But the importance of soil health is much more extensive.

> "Soils are the basis for food, feed, fuel and fiber production and for many critical ecological services,"

explains Ronald Vargas, a Bolivian soil scientist, in a publication of the International Fertilizer Industry Association (IFA) that was published due to the celebration of the World Soil Day and the International Year of soils in 2015. (IFA, 2014, p.2)

Besides its immense role in the water cycle, for filtration as well as for storage and distribution, it is essential for agricultural production and consequently for food security.

According to Vargas ninety five percent of our food is produced directly or indirectly by soils. If we want to meet the fast increasing demand for food, which is estimated to require sixty percent increment of food production, ecological sustainability which ensures healthy soils is necessary.

> "Healthy soils are needed for a healthy life,"

Vargas summarizes.

In addition soil moderates carbon, oxygen and plant nutrition cycle. Storing the major part of organic carbon they are very important to adaption and mitigation of climate change. Of the planet's biodiversity a quarter is found in soils. And they also serve as source for raw material as well as base for constructions. As a fact today unfortunately around a third of the soils are affected by degradation. (IFA, 2014, p.2)

Agricultural interventions, for example drainage, irrigation and application of plant nutrients, alter a pattern of interactions in soil functions: carbon transformations, nutrient cycles, soil structure maintenance, and regulation of pests and diseases. They are all vital for the maintenance of the health of soils, a very complex system with multiple components.

To improve soil health nitrogen (N) fertilizers must be applied, says Dr. Bijay Singh, Indian National Science Agency (INSA) Senior Scientist at Punjab Agricultural University, Ludhiana. This should increase productivity, profitability, cropping system sustainability, and favorable biophysical environment. Otherwise soil acidification is probable, which leads to an imbalance of nutrient availability. On the other hand, N fertilizer application in excess causes deposition of N in areas where it is not dedicated; chronically, this can generate a rise of soil N mineralization. (IFA, 2014, p.3)

figure 5: Women in rice field, nitrogen fertilizers are necessary (IFA, 2014, p.3)

Dr. Amit Roy, President and CEO of the International Fertilizer Development Center (IFDC), indicates that

> "Recent field trials in SSA [Sub-Saharan Africa] show a 50 percent increase in soil productivity when the nutrients are matched to soil characteristics and plant needs." (IFA, 2014, p.6)

This also encourages the adoption of the **4Rs**, a science-based management system explained by Terry L. Roberts, President of the International Plant Nutrition Institute (IPNI). It advocates the

> "application of the right source of nutrient (organic and inorganic), applied at the right rate, right time and right place."

This should encounter the loss of nutrients caused by plant harvest, erosion, leaching and other processes in soils. (IFA, 2014, p.7)

figure 6: ICT support in farmers work today(IFA, 2014, p.5)

To optimize the application of fertilizers and its efficiency the recommendation for its use can be improved in making it more precise and specific depending on soil type, weather conditions and other environmental conditions. To help farmers to make operational and tactical decisions facilitating the responsible and adequate use of fertilizers, crop-soil models should be promoted. Whilst those are currently limited to K, N and P, knowledge gaps with regard to secondary and micro nutrients still exist, as Dr. Prem Bindraban Executive Director of the Virtual Fertilizer Research Center (VFRC) underlines. (IFA, 2014, p.5)

b. Contamination due to agricultural activities

In modern agricultural systems a lot of chemical substances like fertilizers and pesticides are applied to the soil. The overall objective of these chemical additions is to optimize the amount and quality of food and fiber cultivated. Nonetheless often agricultural activities cause environmental pollution in the water, air and land as they are misused and applied in excess. As explained before for example excessive use of nitrogen fertilizer in many cases does not increase their bioavailability but rather results in nitrate pollution of groundwater as it cannot be assimilated by plant completely. (M.L. Brusseau et al., 2006, p.133)

i. Chemical fertilizers

During all their life cycle plants require various chemicals. In an undisturbed ecosystem these elements are provided by the soil solution via mineral weathering, decomposition and death of vegetables (recycling of nutrients), and inputs from the atmosphere as well as from stream deposition. Due to excessive cropping as well as dense monoculture practices plant soil nutrients, in particular nitrogen (N), phosphorus (P), potassion (K) and calcium (Ca) are being reduced. As the crops are harvested, nutrients are being removed from the soil. This over the years resulted in a significant decline of productivity. To counteract this trend, fertilizers are applied to raise the amount of nutrients in the soil again. Most fertilizers contain N, P and K - the so-called macronutrients, as the plants take them up in larger amounts than other essential nutrients.

About the time of World War II improvement of crop varieties and management practices as well as increased mechanization was followed by the dramatically augmented use of fertilizers. However, since the Eighties the use of fertilizers settled down, as concerns about profitability and the environment impact grew. (Artiola et al., 2006, pp.249, 250)

Generally fertilizers are inorganic chemicals. In order they are applied once a year in amounts of fifty to two hundred kilogram per hectar. At highest amount N is added, followed by P and K and in smaller quantities also metals are applied. In the following figure some commonly used nutrient additions are illustrated (Brusseau et al. 2006: pp. 135, 136):

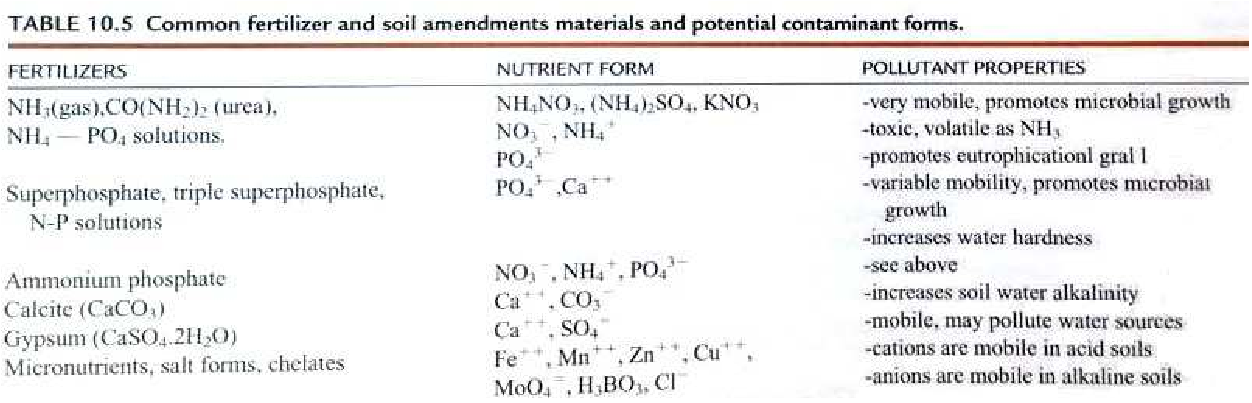


TABLE 10.5 Common fertilizer and soil amendments materials and potential contaminant forms.

FERTILIZERS	NUTRIENT FORM	POLLUTANT PROPERTIES
NH_3(gas),$CO(NH_2)_2$ (urea), NH_4 — PO_4 solutions.	NH_4NO_3, $(NH_4)_2SO_4$, KNO_3 NO_3^-, NH_4^+ PO_4^{3}	-very mobile, promotes microbial growth -toxic, volatile as NH_3 -promotes eutrophicationl gral l
Superphosphate, triple superphosphate, N-P solutions	PO_4^{3-} ,Ca^{++}	-variable mobility, promotes microbial growth -increases water hardness
Ammonium phosphate	NO_3^-, NH_4^+, PO_4^{3-}	-see above
Calcite ($CaCO_3$)	Ca^{++}, $CO_3^{=}$	-increases soil water alkalinity
Gypsum ($CaSO_4.2H_2O$)	Ca^{++}, $SO_4^{=}$	-mobile, may pollute water sources
Micronutrients, salt forms, chelates	Fe^{++}, Mn^{++}, Zn^{++}, Cu^{++}, $MoO_4^{=}$, H_3BO_3, Cl^-	-cations are mobile in acid soils -anions are mobile in alkaline soils

figure 7: Commonly used fertilizers (Brusseau et al., 2006, p.136)

Dependent on the amounts of application, the location where they are applied, and dynamics between soil, plant and water, they can also act as soil pollutants.

Concentration of nitrogen for example is regulated by several factors. Some plants and soil minerals can act as sinks whereas others, as well as animals, the atmosphere and artificial fertilizer additions by humans, can result in excessive N (NO_{-3}) levels. Too high N concentrations can lead to groundwater pollution, which is a cause for methemoglobinemia, also called blue baby syndrome. It occurs in infants and some adults when the digestive system converts nitrate to nitrite. Due to subsequent reactions the ability of blood to carry oxygen is constrained. (Brusseau et al. 2006: p.136)

ii. Animal residues

Under natural environmental conditions and with low animal concentration the amounts of animal waste are not at all harmful to nature. Nonetheless as in the last hundred years animal production more and more turned into large-scale production systems the amount of residues increased to an amount that is not bearable anymore for many environmental systems. Animal-derived contaminants are discharged in concentrated points and are disposed unregulated. Their most common derivatives are nitrate-N, ammonium-N and phosphate-P. As nitrates are very mobile their only controlling factors are plant and microorganism uptake and denitrification. Ammonium in turn is very toxic to fish and after its oxidation to nitrate (nitrification) increases environmental acidity. And thirdly phosphate can lead to eutrophication as already small quantities provoke excessive microbial growth. This raises the biochemical oxygen demand and can be deleterious, especially for stagnant water bodies.

Other pollutants that are released from animal waste are metals (Cu, As, from animal diets and pesticides), other residues of substances to control pests in animal facilities or medicines like antibiotics or growth regulators. (Brusseau et al. 2006: pp.137, 138)

iii. Organic pesticides

In the following figure the major classes of organic pesticides are described. As most of the pesticides are organic compounds this work will concentrate on organic pesticides. However, some forms of inorganic pesticides also exist; they are primarily used to control roaches and rats.

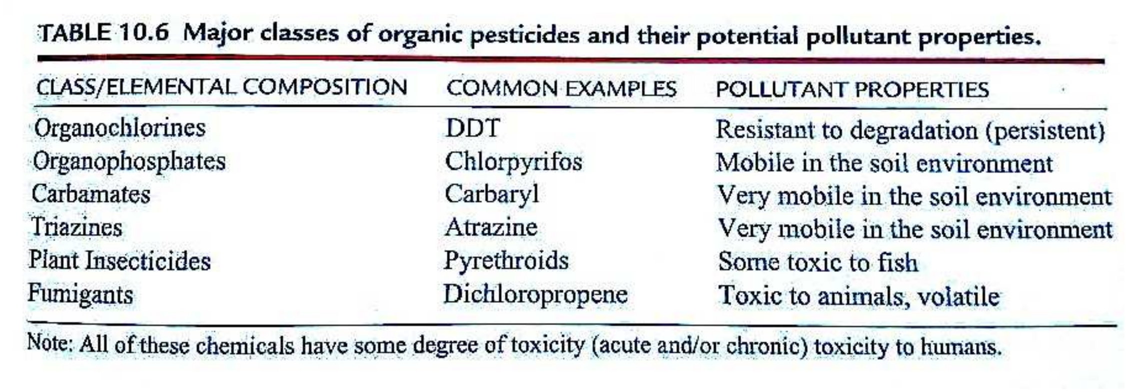


TABLE 10.6 Major classes of organic pesticides and their potential pollutant properties.

CLASS/ELEMENTAL COMPOSITION	COMMON EXAMPLES	POLLUTANT PROPERTIES
Organochlorines	DDT	Resistant to degradation (persistent)
Organophosphates	Chlorpyrifos	Mobile in the soil environment
Carbamates	Carbaryl	Very mobile in the soil environment
Triazines	Atrazine	Very mobile in the soil environment
Plant Insecticides	Pyrethroids	Some toxic to fish
Fumigants	Dichloropropene	Toxic to animals, volatile

Note: All of these chemicals have some degree of toxicity (acute and/or chronic) toxicity to humans.

figure 8: Overview of classes of organic pesticides (Brusseau et al., 2006, p.137)

The water solubility, mobility, environmental persistence, and toxicity are determined majorly by the chemical structure of the pesticide. Pesticide of the first generation where consisted in multiple chlorine groups what broadened there biotoxic effects. This however also meant that they were very persistent and nearly not degradable. The next step was an attempt to make a compromise between toxicity and persistence, toxicity was more targeted and pesticide solubility in water was moderated. Then more soluble pesticides where developed to decrease their persistence in the environment and again their toxicity was specialized. These pesticides are not very attracted to bioaccumulation in humans or animals and their persistence in the environment is very short. However, it is important to apply them properly; their misuse can have various impacts on the environment. The compounds of the triazine family for example today are found very often in water sources in the surface as well as groundwater. In difference, chlorinated pesticides are more often present in soils and sediments and only seldom existent in water. (Brusseau et al., 2006, p.137)

As these organic pesticides are a central aspect of this paper, they are described in detail in the following chapter.

3. Organic pesticides

a. Definition

The term “organic pesticide” can easily lead to some confusion. Therefore the following chapter is an attempt to clear the terminology in this paper.

To start, a variety of **definitions** concerning the terminology are listed:

Due to D.G. Crosby

> “[the] term *organic* is a holdover from the time when carbon compounds were thought to derive only living things.”

Additionally he also states, that often there cannot be determined a fundamental difference in reactivity and physical properties between inorganic and organic compounds. (Crosby, 1998, p.205)

Hari D. Sharma and Krishna R. Reddy 2004 define *organic chemistry* as follows:

> “*Organic chemistry* is the study of compounds that contain carbon. A few exceptions however are CO_2 and related compounds, such as carbonic acids, bicarbonates, and carbonates, as well as cyanides and cyanates. These all contain carbon but are not considered organic compounds. Living systems are made up of organic molecules. In addition numerous organic compounds are produced synthetically.” (Sharma and Reddy, 2004, pp.36, 37)

There also some characteristic properties of organic compounds are outlined:

- Combustibility
- In general low melting and boiling points
- Lower water solubility
- Possibility of several isomers (differently arranged atoms, same chemical formula)
- Molecular reactions and therefore generally slower reactions (than inorganic compounds, typically ionic reactions)
- Multiple bonding due to valency or oxidation state of carbon
- Biodegradability: Source of food for bacteria and other microorganisms

(Sharma and Reddy, 2004, p.37)

On the website of the **EPA** (the Environmental Protection Agency) of the United States the term "pesticide" is defined as follows:

> "A pesticide is any substance or mixture of substances intended for:
>
> - preventing,
> - destroying,
> - repelling, or
> - mitigating any pest."

They also outline that often there is a misunderstanding that it only should include insecticides. However it includes additionally herbicides, fungicides, and various other substances used for pest control. (EPA, 2014)

In the **US-American law** there is also a definition for "Pesticide" available. U.S. Code Title 7, Chapter 6, Subchapter II § 136 (u) defines:

> "The term "pesticide" means
>
> (1) any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest,
>
> (2) any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant, and
>
> (3) any nitrogen stabilizer, [...]. The term "pesticide" does not include liquid chemical sterilant products [...]." (US Code, Title 7, 2011)

Title 7 is also called **Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).**

Defoliants have the effect that leaves drop from the plant and as a result harvest is easier. Desiccants are used to dry up plant material that is not wanted. After the definition of FIFRA many substances can be considered as pesticides, recently developed ones as well as known chemicals. Also included are insect pheromones or sex attractants that are attractive to a certain kind of insects and can confuse their mating behavior. As a result insect populations can be controlled. Additionally ordinary substances like dish detergents to kill whiteflies and bees or table salt (sodium chloride) to control weeds in beet fields in humid regions fall in the category of pesticides after this definition. (Artiola et al., 2006, pp.250/251)

According to the website of the **European Commision**:

> "A **'pesticide'** is something that prevents, destroys, or controls a harmful organism ('pest') or disease, or protects plants or plant products during production, storage and transport.
>
> The term includes, amongst others: herbicides, fungicides, insecticides, acaricides, nematicides, molluscicides, rodenticides, growth regulators, repellents, rodenticides and biocides."

There the difference with the term "plant protection product" (PPP) is emphasized: it is a form of "pesticide" and often is used interchangeably. But actually the term "pesticide" is broader and can also be applied for biocides (e.g. insect repellents, disinfectants and industrial chemicals) (Biocide: European Commission, 2015) whereas PPPs only include uses for plants and corps. (Pesticide: European Commission, 2015)

b. Types of pesticides

One simple way to classify pesticides is to devide them into classes with the same target. For example insecticides are used to control insects, herbicides should erase weed, fungicides suppress fungi such as mold and mushrooms, bactericides kill bacteria. (Crosby, 1998, p. 24)

They can also be classified according to their mode of entry into the pest they should control. The term “contact pesticide” indicates that the chemical is directly applied to the target pest and is also able to enter this way. Systemic pesticides on the other hand must pass through another organism, a “host organism”, before they can enter effectively their target pest. An example could be an insecticide that has to move through the plant system that inhabits the target insect. This also means that an individual insect is not affected by the insecticide if it does not feed on the plant on which the insecticide has been applied. (Artiola et al., 2006, p.251)

The classification used in this work is illustrated in *figure 8* (page 16) and is based on the elemental composition of the pesticide. We distinguish between organochlorines, organophosphates, carbamates, triazines, plant insecticides and fumigants.

i. Organochlorines

Organochlorines, also called chlorinated hydrocarbons, where one of the first classes of synthetic pesticides with mayor importance. Some representatives are DDT, aldrin, dieldrin, endrin, heptachlor and chlordane. Typical properties of these chemicals are the very high insolubility and persistence and they seem to be strongly affected by sorption to the organic matter in soil. As a result of that the rate of biodegradation of these pesticides caused by microorganisms is very low. In contrast to the longevity typical for this class of pesticides, toxaphene, a complex mixture of at least 200 compounds, has only a half-life of nine days (Kearney and Roberts, 1998, p.45/52)

As already said one of most significant organochlorine pesticides is the insecticide DDT. It was developed in World War II. In the beginning it was no short time effect and it only had the effect to kill the insects. In this time, scientists thought that a chemical compound can only be transported if water-soluble. DDT didn't have this characteristic and therefore it seemed to pose no environmental risk.

Later it was realized that it has long term effects on other organisms, like increasing incidence of cancer or affecting the ability of birds to produce eggs. Also it was discovered that it is likely to be stored in fats and oils. This not only allows DDT, despite not water soluble, to be transferred biologically, but also meant that the higher an organisms is on a food chain, the higher DDT is concentrated in its body. This effect is also called "food chain concentration" or "biomagnifications".

To respond to these discoveries, DDT was banned in most developed countries. In the USA for example it was banned in 1971 and since then it has been very significant how birds recovered. Still DDT is produced in the United States of America to be sold to more developing countries where the use of DDT against malaria-spreading mosquito is still very usual. (Botkin and Keller, 2003, p.219)

Also, after the broad revelation of residues of many other organochlorines in the environment in the United States the use of most of these insecticides was cancelled. However, before that over a period of twenty to thirty years a huge amout of these persistent insecticides have been used in numerous crop protection and public health programs and soil and water remediation of contaminated areas has been a big challenge. (Kearney and Roberts, 1998, p.53)

ii. Organophosphates

Due to Senesi and Chen (1989) in comparison to chlorinated hydrocarbons (e.g. DDT, toxaphene, lindane …) organophosphates are a lot more toxic, especially their toxicity to humans is very high. However, their persistence in the environment is generally lower. This should be seen in relation with higher water solubility and greater vapor pressure of the organophosphates. Examples for this type of chemicals are the insecticides malathion and parathion, known to be processed by chemical hydrolysis and biodegradation of microorganisms, or the herbicide glyphosate, which after Senesi and Chen (1989) is one of the most used herbicides. (Yaron, Calvet and Prost, 1996, p.45)

iii. Carbamates

Originally scientists' general opinion was that carbamates have a lower toxicity than phosphates. Indeed carbaryl (Sevin®), the first commercially successful insecticide of the class of carbamates, seemed to have quite favorable toxicity concerning mammals. Then other compounds arrived, like aldicarb (Temik®), which unfortunately was toxic to mammals. Actually it is one of the most mammalian toxic insecticides. Later also carbaryl was proved to be very toxic to bees and various aquatic invertebrates. This posed a hazard enhanced by the low metabolic detoxication rate and moderated only by the environmental hydrolysis. (Crosby, 1998, pp. 295-296)

Actually the importance of hydrolysis as biotransformation reaction of carbamates in humans and bacteria is very high. A lot of vertebrate depend on oxidation for sixty to eighty percent of their carbon detoxication. Insects rely on it for eighty to ninety percent and plants for one hundred percent. Aldicarb sulfoxide and sulfone remain in soil for long periods, but thanks to hydrolysis and photo oxidation most carbamates residues in the environment are negligible. (Crosby, 1998, pp.295-296)

iv. Triazines

Some members of the family of triazine pesticides count as herbicides that are used most extensively in North America. Atrazine actually is applied in two thirds of the cultivated areas of the United States like corn and sorghum fields and even ninety percent of sugarcane cultivations. Another member of this family of herbicides is Simazine. Presently is application to a numerous fruits, vegetables, nuts, turfgrass, and conifers is common; in total it is applied to thirty high-value crops.

Although there is little knowledge about the toxicity of this class of pesticides to human as well as to nature, they are used widely. Regarding atrazine it can be said that its toxicity to fish is very low and also its risk to be bio accumulated is quite small as it is very susceptible to rapid degradation to less or even nontoxic derivates. (Gross et al., 2003, p.1063)

v. Plant Insecticides

An example for plant insecticides is pyrethroid. It is seen as non toxic to mammals (Sotherton and Holland, 2003, p.1186) but toxic to fish. Due to studies of exposure of pyrethroid in fish, an increasing toxicity with reduction in the water temperature has been proved. The thermal effects with permethrin, a synthetic pyrethroid, exposed on the rainbow trout are one of the most significant. This means that higher temperatures are more protective for the trout regarding this compound.

Studies on the effect on amphibians have not been so clear. As exposed to some pyrethroids a dramatical increase of lethality of *Rana pipens* adults was observed at cold temperatures of 4°C in comparison to 20°C. Also, behavioral observations of young tadpoles of *Rana clamitan* and *Rana pipens* after sublethal exposure to permethrin and also fenvalerte revealed that they recovered more slowly at temperatures of 15°C than at 20°C. However, lethality of esfenvalerate in tadpoles of *Rana spp.* was seen to be lowered by moderately cool temperatures of 18°C compared to 22°C. (Rattner and Heath, 2003, p.683)

vi. Fumigants

Fumigants are pesticides applied in gaseous form. They may be used to control particular termites in drywood of houses or populations of pests in storage rooms, in products like fruits, vegetables and grains. It is also possible to apply them to control pest in soils over large areas. (Artiola et al., 2006, p.251)

4. Mathematical modelling of pesticides fate and transport in the environment

a. General processes of contaminant transport and fate in the environment

To be able to evaluate fully the potential impact of contaminants in the environment and thus also on human health, we need to understand as good as possible the transport and fate of contaminants. Knowledge about these processes is for example very important to estimate the probability of a contaminant to pollute surface or groundwater and with this information later to plan adequate risk assessment. Further on such calculations are necessary for the development and evaluation of remediation methods for environmental pollution. Additionally this information can help to design and develop chemicals that are the least possible to contaminate the environment and to minimize the potential of human health impacts.

Generally contamination of the environment is dominated by four processes:

Advections, **dispersion**, **interphase mass transfer** and **transformation reactions**.

These processes are discussed in detail below. Their combination determines the fate of a specific contaminant in and its potential impact on the environment. The result of these estimations is the "pollution potential" and "persistence".

Pollution potential could also be describes as the "ability" of a specific contaminant to pollute the medium of interest, which can be water, air or soil. If a contaminant for example is transported immediately, e.g. due to its high water solubility or low sorption probability, and not very likely to be transformed to any great amount its pollution potential is higher.

On the other hand a low transformation potential also means a higher **persistence** of the contaminant. The chemical remains precarious for a longer time.

The function of those two contaminant properties, pollution potential and persistence, give an idea of the human health risk associated with a chemical. The greatest risk, for example, is posed by a contaminant with high persistence and at the same time elevated toxicity. (Brusseau, 2006, pp. 79, 80)

In general the physicochemical properties of the contaminant have a major influence on transport and fate behavior. The higher the vapor pressure of a contaminant for example, the higher is the probability of it to evaporate or volatilize into the gas phase and hence to be transported in the atmosphere. This type of transport can also occur in the vadose zone, the area limited by the land surface and the water table. Other significant properties that may influence the movement of a contaminant in the soil and groundwater are water solubility, biodegradability and the phase state. Last one is considered to be a very critical property as the mobility of a contaminant depends partly on this characteristic. Naturally contaminants can occur as solids, liquids or gases. In general gases are recognized as the most mobile and solids as the least mobile.

One big problem is posed by nonaqueous-phase-liquids (NAPLS) such as fuels (gasoline and aviation fuel), chlorinated solvents and polychlorinated biphenyls. They are referred to be immiscible organic compounds that under standard conditions occur as liquids. Their physical remediation is very complicated what forms them into a long-term contamination source.

Inorganic compounds mostly occur as solids in their elemental state, but they can also often be found in ionic form (e.g. Pb^{+2}, Cd^{+2}, NO_3-). Their speciation highly influences solubility in water and sorption potential. One exception is mercury, which under natural conditions is in liquid phase. (Brusseau, 2006, pp. 80, 81)

i. Advection

Probably the primary mode of transport of a contaminant in the environment is advection and is the most important reason for contamination movement at large scale. It describes

> "the transport of matter by the movement of a fluid." (Brusseau, 2006, p.79)

This movement is determined by the gradient of fluid potential. A solute, a contaminant dissolved in water, for example can be either transported through the soil (infiltration) or above it (runoff). In the same way contaminant molecules in the air, where they appear in vapor phase, are carried along with the air flows.

The bulk transport that occurs due to advective processes is mainly characterized by the rate and direction of the fluid movement. Defining the air and water movement in subsurface is very complex. For the characterization of groundwater flows for example generally groundwater maps are required. One important aspect in these studies is the measurement of groundwater velocity, which for instance can be determined by *Darcy's Law*. This approach estimates the average pore-water velocity using the hydraulic conductivity and the hydraulic gradient. (Brusseau, 2006, pp. 81, 82)

ii. Dispersion

Another way of transport in water as well as in air is dispersion, which is described as

> "spreading of matter about the center of the contaminant mass."
> (Brusseau, 2006, p.82)

In general movement of a contaminated mass better said the movement of its "plume" or "pulse" is dominated by advection, but additionally the size of the plume grows due to dispersion. This type of transport is primarily the result of molecular diffusion and secondly non uniform flow fields.

The cause of molecular diffusion is random motion of individual molecules. As every molecule vibrates and moves as a result of its kinetic energy, each molecule can spread at any given time in an arbitrary direction – random motion is generated. Typically molecules move from area with higher molecular concentration to areas with lower concentrations, where there are fewer molecules. To visualize the effect of dispersion, a drop of food color in glass of water can be used – it will spread randomly and in the end color the entire water-volume.

Normally the contribution of dispersion to the overall transport of contamination is small, but in areas where advection is minimal, for instance in the saturated zone of the subsurface in clay units, it can become significant.

In the end dispersion is mainly caused my non uniform flow fields. A fluid mass moving through the environment does not move in one defined body but rather spreads with parts in different velocities. There are some observations that can be made concerning dispersion and velocity distribution:

Generally molecules of fluids near a wall in a channel of a river move slower than molecules in the center. This is caused by **friction**.

In the subsurface at **small scale**, which describes areas of under one meter, dispersion is majorly caused by three different ways of non-uniform flows:

- Due to friction in a **single pore** the flow is also faster in the center than near the walls of the pore.
- Differences in the flow velocity are also determined by the **pore-size distribution**. In larger pores the velocity is generally higher than in smaller ones. This also is caused by the influence of friction which proportionally is less in larger-diameter pores.
- Flow is affected by the **tortuosity** of the soil area. A less tortuous flow path means that the path has fewer turns and twists and the molecules can move faster from one location to the other, their travel distance is shorter.

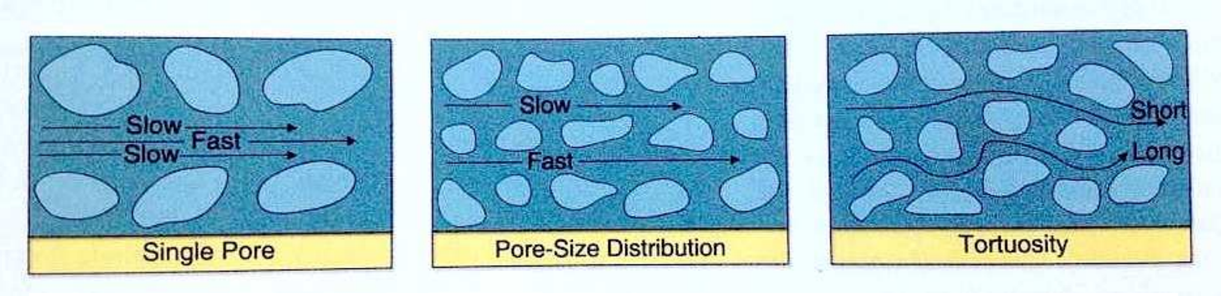


figure 9: Three major ways of dispersion (Brusseau, 2006, p. 82)

Concerning **large-scale-areas** - means when we look at a whole field - fluid velocity is primarily determined by the **permeability** of the soil. Sand for example is much more permeable than clay and therefore fluids move faster in sandy areas. Finally the movement of different sections of the pulse at different velocities results in the spreading in the direction of travel. (Brusseau, 2006, pp. 82, 83)

iii. Mass transfer

As explained previously, a contaminant can exist in the air, in the water or associated with a solid phase. Transporting a contaminant from its original phase to another one is primarily generated due to four processes: dissolution, evaporation, volatilization and sorption.

Dissolution can also be described as

> "the transfer of molecules from their pure state to water." (Brusseau, 2006, p.83)

If for example salt crystals are put into water, after some time they will get dissolved in water – the result is dissolution.

The extent to which the contamination of water occurs depends on the aqueous solubility of the molecules. The **solubility** of organic compounds in water is governed by the ability of the molecules to interact with water. As water is a highly polar solvent this aspect depends very much on the polarity of a molecule. The aqueous solubility of ionic or polar organic contaminants is high compared to the one of non-polar compounds. Comparing phenol, a highly polar compound, with toluene, a highly non-polar one their solubility varies by the factor 159. Additionally there are other factors that can affect the solubility, such as temperature, salinity or the presence of alcohol or detergents (surfactant). Generally organic compounds are more soluble at higher temperatures, but for some of them the opposite is true. Concerning the effect of alcohols and surfactants in contamination mixtures, their presence increases the amount of contaminant in solution. They are added to gasoline to raise oxygen content and are also used as basis for subsurface remediation. (Brusseau and Chorover, 2006, pp.95, 96)

The solubility of inorganic compounds is described by the "relative saturation Ω" of the system. It depends on the equilibrium of the reaction between precipitation and dissolution. If Ω is minor to one, the solution is called *undersaturated* and dissolution will occur. If Ω is mayor to one the solution is termed *supersaturated* and precipitation will take place. If the solution is in equilibrium, which means that Ω equals one and neither precipitation nor dissolution appear, the solution is called saturated. (Brusseau and Chorover, 2006, p.94)

If water is contaminated by a compound it also depends on the *pollution action level* of the compound. This means that concerning compounds with a small maximum contaminant level, even though only a small amount of pollutant is released, this level can already be exceeded. (Brusseau, 2006, p.83)

Another process of mass transfer is **evaporation**. When a compound evaporates, it transfers from its pure liquid or solid phase to gas phase. To describe the rate at which a compound will evaporate vapor pressure can be used. Vapor pressure equals the pressure of gaseous contaminant in equilibrium with liquid and solid phase of contaminat. In the vadose zone, where some pores are filled with soil gas, this type of transport may be important when there is pure-phase contaminant present, which can evaporate easily in the soil atmosphere.

Evaporation is primarily dominated by contaminant-contaminant interactions, rather than interactions between contaminant and water. This derives from the low inter-molecule interactions of gases, where molecules have a lot of space between each other. Vapor pressure for gases therefore is very high, and the one of liquids are generally higher than the ones of solids. What is more is that temperature has a significant influence on vapor pressure as it is an important factor concerning gas-phase interactions. (Brusseau and Chorover, 2006, p.96)

In contrast to evaporation, **volatilization** means that a contaminant is transferred between water and gas phase. The difference is that evaporation specifies on the molecule transfer from their pure state, whereas transfer due to volatilization evolves from water, where the contaminant is dissolved, to the atmosphere. Similar to its role in evaporation, in volatilization vapor pressure is more or less an indicator for its degree, but additionally the rate of volatilization depends on the solubility of the component and environmental factors. In the vadose zone volatilization is an important component for transport as well as for remediation. To describe the distribution of a contaminant between gas and aqueous phases at equilibrium we use *Henry's Law,* which depends on the concentration of pollutant in gas phase as well as in water phase and the *Henry's constant*, a dimensionless contaminant-specific value that is also influenced by temperature. (Brusseau and Chorover, 2006, pp.96, 97)

The fourth of the primary processes that influence mass transfer is **sorption**: it describes the process of molecules of a contaminant being associated with the solid phase of porous medium (in this case mainly soil particles). There are several mechanisms that determine the rate of sorption: properties of the contaminant as well as the ones of the sorbent and the solid phase, to which the contaminant sorbs, are important factors. Thus the surface of the soil and sediment has a significant impact on the sorption rate. Inorganic pollutant attraction for example depends largely on the charge properties of the surface particles.

In this transfer mechanism adsorption and desorption are distinguished. Adsorption on the one hand describes the accumulation of molecules at the sorbent and simultaneously their removal from the aqueous solution. Desorption on the other hand is termed the process when adsorbed particles (also called the adsorbate) are released into the aqueous solution. Some of the ions are attracted to soil due to electrostatic forces, when this interaction can be disrupted easily, they can be called "exchangeable". Then they are also considered "bioavailable", which makes them an important source for microbial or plant uptake. To describe the extent of this exchange the terms *cation exchange capacity* (CEC) and corresponding *anion exchange capacity* (AEC) are introduced. They define the quantity of moles of exchangeable cation or anion charge a unit mass of soil or sediment is able to absorb.

The association of organic contaminants depends highly on the interaction with organic material, which is generally less polar than water and thus the environment is more favorable for nonpolar organic contaminants. It is also called "hydrophobic effect" as its mayor driving force is the organic compounds incompatibility with water. Sorption of polar or ionic organics is influenced mainly by the same mechanisms as the one of inorganics. As most of the ionic organic compounds are negatively charged they are mostly repulsed by soil and sediment particles, which have also a net negative charge. The result is a low sorption rate of these particles. However the number of positively charged particles (e.g. Fe and Al) that are adsorbed should not be underestimated.

In the end, besides the properties of the contaminant itself (nonpolar/polar, inorganic/organic …) physical and chemical properties of a sorbent are also very important. Amount of organic matter, exchange capacities, clay content, and metal-oxide content are some of the most determining ones.

To quantify sorption a sorption isotherm is used, which relates the concentration of the contaminant in the sorbed state and the concentration in the aqueous state. The simplest way to describe this relationship is the *Linear Isotherm*. It describes that the concentration of sorbed contaminant will always be proportionally the same as the concentration in the water. Many nonpolar organic compounds are sorbed linearly, but some organic and most inorganic compounds show nonlinear sorption. A nonlinear isotherm means that distribution of contaminant between dissolved and sorbed phase varies proportionally at different concentrations. In those cases the *Freundlich Isotherm* K_f can be used. (Brusseau and Chorover, 2006, pp.97-101)

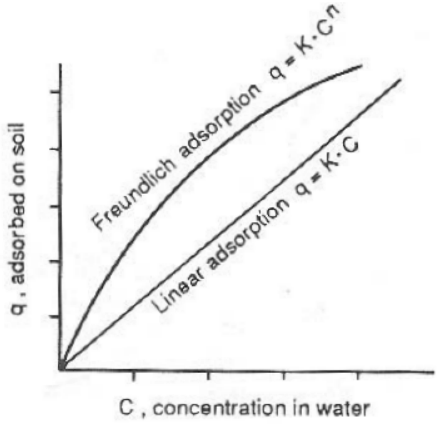


figure 10: A Comparison of a Linear and a Freundlich Isotherm (Raymond Henry, 2015)

Figure 10 shows the difference between a sorption that is determined by a *linear isotherm* and one that actuates due to a nonlinear isotherm, in this case the *Freundlich isotherm*.

Contaminant molecules sorbed to grains are immobile as long as the grains itself are immobile. Contaminants that do not sorb move generally at water velocity through the soil, but as sorption increases the velocity of the contaminant flux decreases. This deceleration of the rate of movement of contaminants is also referred to as "retardation". (Brusseau, 2006, p.83)

iv. Transformation reactions

Other ways, in which transport and fate of contaminants can be influenced, are transformation reactions. Usually the result of such reactions is positive, as they mostly reduce the amount of actual pollution compared to the one that would be possible in the environment. In some cases, however, the result can be negative, as the transformation reaction may lead to an even more dangerous and precarious compound. (Brusseau, 2006, p.83)

One important transformation reaction for example is **hydrolysis**. As water is a ubiquitous component in the environment nearly all of the contaminant will have contact with water at some point. If a contaminant reacts with water this is called hydrolysis. Important factors in hydrolysis reactions are the pH of the soil and the charge properties of the contaminant. (Brusseau and Chorover, 2006, p.101)

Another group of key reactions concerning transfer are oxidation-reduction-reactions, generally referred to as **redox reactions**. These reactions can take place wherever the two species involved are inorganic, organic, liquid, gaseous or solid. During a full reaction one of the components is being reduced. This means it enters in its more oxidized form and accepts at least one electron. The other components is being oxidized, which means it begins the reaction in its more reduced form and losses one or more electrons. Microorganisms can function as catalyst, but in the end the reaction only takes place if thermo dynamical conditions are favorable. (Brusseau and Chorover, 2006, pp.101, 102)

In the top few centimeters of surface water and land surface as well as in the atmosphere exist some compounds that can be transformed under the influence of the energy of sunlight. The term for transformations under the influence of light energy is **photochemical processes**. Often they result in redox reactions, which have been discussed in the paragraph above. To be able to react in photochemical ways a molecule needs to be capable to absorb photons, a quantity of light energy (in Joules, J).

Organic as well as inorganic pollutants can be transformed by indirect or direct photolysis. Direct photolysis is a reaction called, where the light absorbing substance itself is transformed. The characteristic of this photo activation is that an electron transits to a higher state, which increases the susceptibility of the contaminant molecule to be transformed. Indirect photolysis is called the reaction of contaminants with photolysis products when the compound that is transformed is not absorbing the light itself. The light energy that induces their transformation derives from a reactive photolysis product such as hydroxyl radicals, ozone and singlet oxygen. (Brusseau and Chorover, 2006, pp.102, 103)

Another transformation that takes places rather spontaneously is **radioactive decay**. It is important for radioactive elements. Instability of the nucleus in the atom generates it and simultaneously causes radiation. There are different types of radiation: emission of an alpha particle (two neutrons and two protons) – alpha radiation; emission of an electron – beta radiation; and emission of an electromagnetic pulse (gamma ray) – gamma radiation. (Brusseau and Chorover, 2006, p.103)

The overall process of biological transformation is **biodegradation**. It can be describe as breakdown of organic compounds due to activity of microorganisms. An important aspect of biodegradation is the bioavailability of such organics, which means their availability for microbes as food source, or substrate. It is highly dependent on the concentration of content in water phase, as the microbes obtain their food from the water surrounding them. Thus low water solubility, like for example gasoline, and a high sorption rate of the substrate by soil are important factors, that have an reducing impact on bioavailability and hence biodegradation. (Maier, 2006, p. 106)

v. Estimation of phase distribution

As discussed before, contaminants can exist in different phases in the environment: they residue either as vapor in air, dissolved in water or sorbed to the soil. The distribution of the contaminant between these phases is often a key factor when estimating the movement of a contaminated mass. One of the simplest ways to estimate this distribution is to apply phase-distribution coefficients. They illustrate the concentration ratios between two phases and thus give information about how the contaminant is distributed between those two. The *sorption coefficient* provides information about the distribution of the contaminant between water and porous-medium particles. The *Henry's Constant* helps to determine the distribution between water phase and gas. These coefficients may help us to define important information, like for example the total amount of contaminant in a system. (Brusseau, 2006, pp. 85, 86)

b. Governing equations

i. Overview of equations

As described in the chapter above there are various processes that determine the transport and fate of a contaminant in soil. To estimate the result of these processes a series of equations is needed to set up an adequate mathematical model. It is important to say that the accuracy of this mathematical model as representation of the real world always depends on the validity of the input parameters and the assumptions as well as the representativeness of the simplifications. Transport of contaminants in the environment is very complicated; therefore the grade of representation formed by different equations depends a lot on their complexity. In the end the mayor limiting factor for us to use more complex equations to describe these processes in reality is the need to determine values for all the unknown parameters. This can be very difficult, expensive and time consuming as the site has to be characterize in detail. (Brusseau, 2006, pp.86,87)

ii. Advection-dispersion-equation

The advection-dispersion equation is one of the most widely used equation for the representation of transport and fate of pollutants in the nature. It can be used to describe transport of a solute in porous media in a relatively simple way. In “Environmental Pollution Science” (Brusseau, 2006, p.87) a simplified version of this equation can be found:

$$R\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - T \qquad (1)$$

where

C =...contamination concentration

D =...dispersion coefficient

R =...retardation factor (discussed in chapter iv.)

T =...represents possible transformation reactions

v =...mean fluid velocity

t =...time

x =... distance

For this equation various assumptions must be taken into account, for example fluid flow is assumed to be uniform and one-dimensional, media conditions are homogenous and the only mass transfer process considered is sorption.

Change of the amount of contaminant at a given point in the media is represented by the term on the left-hand side. These changes occur due to advection and dispersion, which cause transport of the contaminant, and mass transfer and transformation reactions. With the first term on the right-hand side advection is described. The second one represents dispersion. For the representation of all possible transformation processes the term T is used. For the estimation of these processes the "first-order" reaction (first order reaction depend linearly on only one reactant concentration (Curtis, R., Cathy Nguyen, C. Lower, S., 2015)), which is discussed in detail in the following chapter, can be used. (Brusseau, 2006, pp.86-87)

iii. Quantifying Transformation Rates

To quantify transformation rates, the **first order equation** can be used:

$$\frac{\partial C}{\partial t} = -kC \qquad (2)$$

where

C =...contaminant concentration

t =... time

k =... transformation rate constant [1/T] (Brusseau and Chorover, 2006, p.103)

With this equation it is stated that the rate of transformation depends on the quantity of contaminant present. As concentration changes of the contaminant are negative a minus sign is necessary (on the right-hand side), it illustrates that with the time concentration of reactants goes down. With this equation fixed pH-hydrolysis, radioactive decay and biodegradation can be described.

Another important factor to describe transformation processes is a *half life* ($T_{1/2}$). It defines the time after which half of the amount of the contaminant is transformed. If a contaminant follows first-order kinetics its *half life* can be described by the following equation:

$$T_{1/2} = \frac{0{,}693}{k} \qquad (3)$$

where

k =... transformation rate constant [1/T]

With this equation it can be estimated how long the transformation of a contaminant takes in the environment. It also helps to determine the persistence of the contaminant. For example after ten half-lives, less than 0.1% of the original amount of contaminant remains in the medium. Of a contaminant with a half-life of one day for instance after ten days 0.1% of the initial contamination mass should be transformed. (Brusseau and Chorover, 2006, p.103)

iv. Retardation factor

$$R = 1 + \frac{\rho_b}{\theta} K_d = \frac{v_w}{v_p} = \frac{d_w}{d_p} \qquad (4)$$

where

ρ_b =… bulk density [g/cm^3]

θ =… soil-gas constant, volume of soil gas per volume of soil

K_d =… sorption coefficient [mL/g]

v_w =… velocity of fluid

v_p =… velocity of the contaminant

d_w =… distance traveled by the fluid

d_p =… distance traveled by the contaminant

The equation above describes the *retardation factor*, which represents the effect of sorption on transport. Observing the equation it can be seen that if the sorption (the sorption coefficient) grows, retardation grows too. Also it indicates that if there is no sorption (K_d=0) *retardation factor* is one and velocity of the contaminant equals velocity of the fluid. If for example R=10 it means that contamination moves at one-tenth of the velocity of the fluid. Contaminants with a retardation factor of ten or smaller are considered to be relatively mobile, this means that they can move very rapidly from the point they where spilled and can contaminate a large area in short time. Conversely, contaminants considered with high *retardation factors* (1000 or higher) move slowly in comparison to the fluid and the extension of the contaminated zone is generally smaller than the one affected by mobile contaminants.

There are also cases where retardation factor can be smaller than one, which would means that the velocity of the contaminant is faster than the fluid in which it is present. This can primarily happen due to the effect of the so called "*anion exclusion*": An anionic substance (e.g. Cl^-) enters into the subsurface, which mostly has a net-negative charge. As a result the negative charged solutes are repulsed and do not enter in part of the water residing in the pores. Thus the contaminant will only travel through a portion of the soil and its transport velocity appears higher than the one of the fluid in which it is being carried. Another cause for retardation factors smaller than one is *size exclusion*. If the contaminant molecules are very large (e.g bacteria and protozoa), they cannot enter in all the pores accessible for the fluid and as a result of that the molecules can only travel through a portion of the soil. As in the case above this means that, even though individual solute molecules are actually not moving faster contaminant transport appears more rapid than the rate of fluid movement. (Brusseau, 2006, p.86-87)

c. Available models

i. Overview of models

The increasing amount of threats to soil and waters that were discussed in *Chapter 2*, make prediction of transport and fate of contaminants necessary. One way to do this, are mathematical models. In the beginning models for one dimensional transport, homogenous media and very simple boundary conditions were used. As knowledge of solute behavior in soil and computer performance got better, complexity of these models increased too. Now not only processes of transport can be taken into account more detailed, but also the output can be illustrated two- and three dimensionally. (Yaron, Calvet and Prost, 1996, p.265)

Besides PESTAN from the US EPA, which is described in detail below, in the following chapter some models to estimate fate of pesticides are listed. They are developed by scientists from *Wageningen University and Research Centre* (WUR), the *National Institute of Public Health and the Environment* (RIVM) and the *Netherlands Environmental Assessment Agency* (PBL). They should help to make an adequate evaluation of environmental fate of plant protection products. These models are used for registration of plant protection products on a European and national level and are internationally known for high quality. However, in difference to PESTAN they are mainly used to calculate fate of pesticides and other compounds in the surface water. (WUR, RIVM, PBL, 2014)

ii. Pestan

PESTAN (Pesticide Analytical Model) is a computer code for calculating transport of organic solutes passing through soil to groundwater. The original model was developed by Enfield et al. in 1982 and since then has been used by the *Office of Pesticides Program* by *The United States Environmental Protection Agency* (EPA) to estimate potential for groundwater contamination of currently registered pesticides and those submitted for registration. The calculations are based on a closed-form analytical solution of the *advective-dispersive-reactive transportation equation*; furthermore the model has been tested various times under field and laboratory conditions (Enfield et al., 1982; Jones and Back, 1984; Melancon et al., 1986). (Ravi and Johnson, 1982)

Conceptualization

A dissolved pollutant that is transported vertically through the vadose zone is replicated in the model as a “slug” of contaminated water. Therefore the concentration of the chemical slug is equal to the water solubility of the pollutant and its thickness correspond to the volume of pore water that is used to dissolve the total available mass of pollutant depending on the solubility of the pollutant.

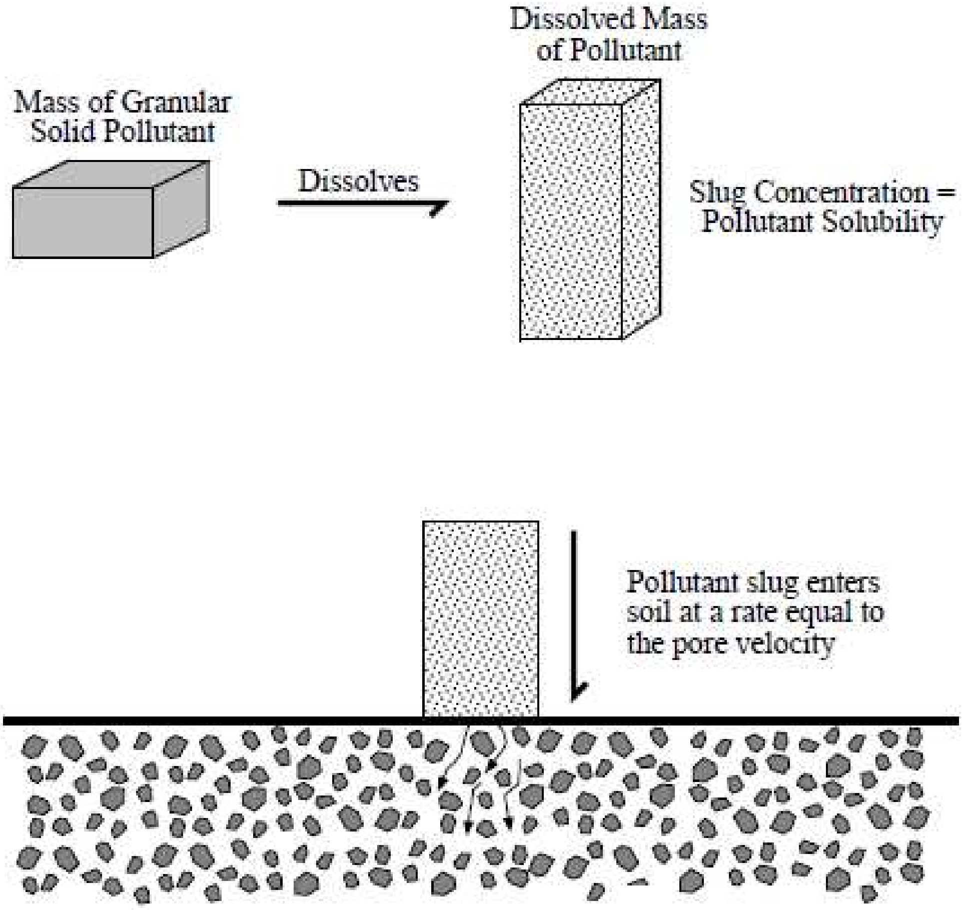


figure 11: PESTAN conceptualization (Ravi and Johnson, 1982, p.11)

Defining the mass of pollutant dissolved entering the soil two different cases must be considered. If the time of application coincidences with the time of recharge the dissolved mass of pollutant entering equals the mass applied. But if there is a time lapse between the application and the recharge event some of the mass applied will be lost due to solid-phase decay. It describes degradation (photodecomposition and volatilization) of the pollutant at the surface before it enters soil and begins at the time of application.

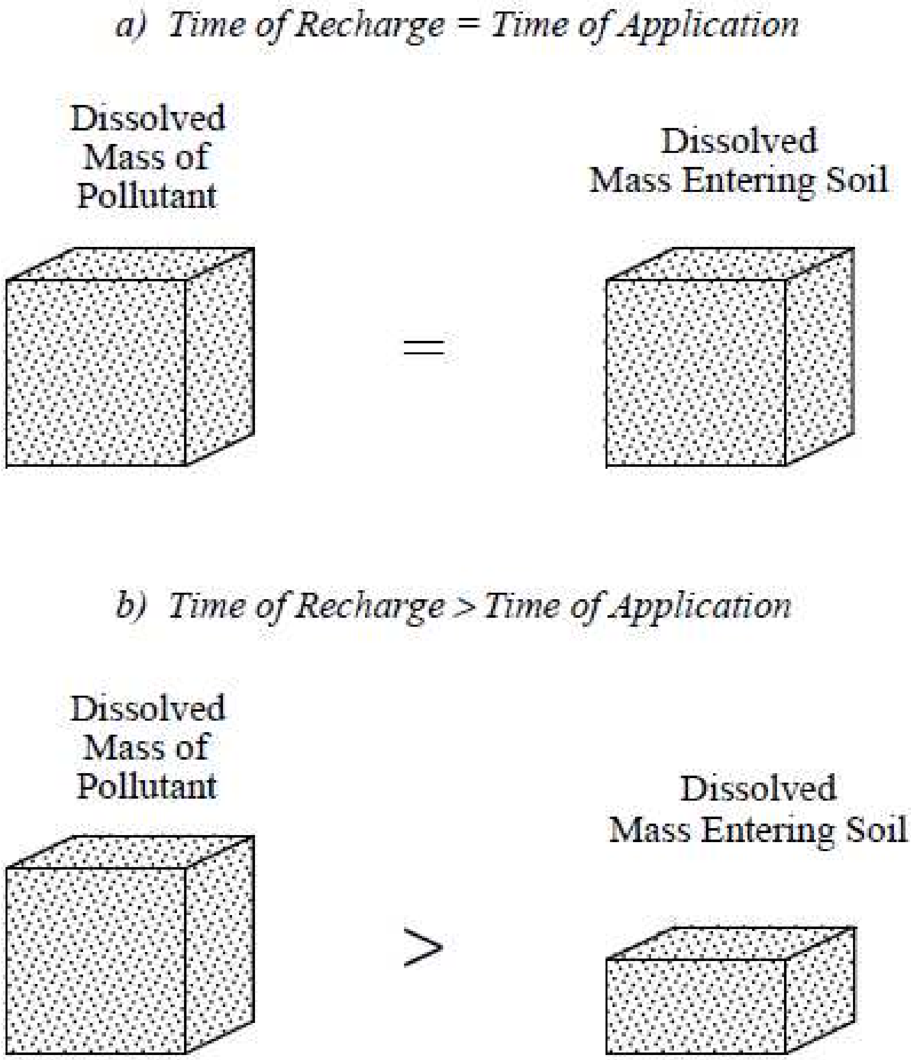


figure 12: Application of Slug (Ravi and Johnson, 1982, p.12)

After the application the slug begins to infiltrate the soil with the first event of recharge (precipitation, irrigation) at a velocity equal to the pore water velocity. Once in the soil the solute is influenced by dispersion and sorption. Other possible forms of alterations of the mass of pollutant are liquid-phase decay (microorganisms) and migration out of the soil domain. (Ravi and Johnson, 1982)

Assumptions

Based on the assumptions made by Enfield et al. (1982) the following aspects should be considered to fully understand the development of the PESTAN model:

- The soil domain is dominated by steady-state flow conditions. During a rainfall event flow requires some time to develop those conditions, dependent on the soil texture. Due to Philip's Work (1969) for example clay rich soils need forty eight hours whereas in sandy soil steady state conditions are established in less than an hour. This could cause an error in simulations prior to reaching steady state conditions.
  Also in the description of the relation between water content of the soil and hydraulic conductivity by Campbell (1974) those conditions are assumed.

- The concentration of pollutant in the leak water is assumed to be the maximum possible concentration. This means on the one hand a minimum slug thickness, which results in a thinner pollutant concentration profile in the soil, and on the other hand that pollutant concentration will be estimated higher than actually occurring in the soil.

- Also the assumption mentioned above that the dissolution enters soil at pore water velocity can cause results not coherent with the true ones. If the values for the pore water velocity are measured indicating a recharge rate which incorporates losses due to evaporation or is calculated as an average over longer periods, the recharge rate and hence the velocity value will be considerably less than during an actual rainfall event. This means that the simulations will show a slug moving slower than under true conditions.

- Even though it rarely occurs in the field, homogenous soil properties are assumed in the model. To avoid a false estimation considering the impact of non-uniform soil a range of simulations covering the different soil conditions in the area observed should be compared.

- The distribution of the pollutant between solid and liquid phase is described via linear isotherms which presumes that those phases are in a local and instantaneous equilibrium.

- Solid phase degradation as well as liquid phase degradation, which occurs within the soil, are considered to cause first-order decays. This assumes that the rate of liquid phase degradation do not vary with soil depth, what actually can occur for example due to biological activity.

- No non-aqueous phase liquids or any flow conditions derived from variable density are taken into account in the model.

Equations

The mathematical model of this program is established with a few modifications, on the formulation of Enfield et al. (1982). Their calculations are based on the one-dimensional differential equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} - \frac{\rho}{\theta}\frac{\partial S}{\partial t} \qquad (5)$$

where

C =… pollutant concentration in the liquid phase [mg/l]

t =… time [hrs]

D =… dispersion coefficient [cm^2/hr], can be ignored if the shape of breakthrough is no required, thus the equation can be simplified without reducing the accuracy

V =… interstitial pore water velocity [cm/hr]

x =… distance along the flow path [cm]

ρ =… bulk density [g/cm^3]

θ =…. Volumetric water content (volume of pore water/total volume) $0 \leqslant \theta \leqslant 1$ [cm^3/cm^3]

S =… sink or source term [μg/g].

To solve problem (5) the following initial and boundary conditions are implemented:

$$C(x=0,t)=g(t)$$

$$C(x,t=0)=0$$

$$C(x=\infty,t)=0$$

The description of the sink or source term is the main requirement concerning inputs. It can adequately be approximated by a linear or *Freundlich* isotherm coming from the equation

$$S_r = K * C^n \qquad (6)$$

where

K =… sorption coefficient

n =… Freundlich exponent

r =…denotes retardation component of sink/source term. (Enfield et al., 1982)

In soil systems degradation is caused by abiotic as well as biological processes. In the equations of Enfield et al. it is assumed that it can be described following first-order kinetics although most processes in the environment follow pseudo first-order or second order kinetics (sum of exponents equals two). This means that there are environmental constraints for which reason a single value may not be sufficient.

The result of the inclusion of different degradation processes (volatilization, hydrolysis and other abiotic and biotic processes) is a general equation to describe the transport of organic pollutants in soil, which can be elevated in several different ways, is described more detailed in the original paper by Enfield et al. (1982).

In aforesaid paper sensitivity of this equation to the degradation and therefore an accurate determination of this parameter are emphasized.

The formulation of Enfield et al. (1982) has been modified as follows to adopt as mathematical model for PESTAN as follows:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} - \frac{\rho}{\theta}\frac{\partial S}{\partial t} - k_1 * C \qquad (7)$$

The parameters correspond to the one in equation (5) save to S and k_1 in equation (6)

S =… solid-phase concentration (mass of pollutant in soil/mass of soil) [g/g]

k_1 =… first-order decay coefficient in liquid phase (/hr).

In this model $\partial C/\partial t$ describes the rate of sorption of pollution from the liquid phase to the solid phase. Further considerations are described in the PESTAN guide. (Ravi and Johnson, 1982)

Input Parameters

Consecutively the input parameters are described, the model itself does not account any uncertainty of these parameters:

Water Solubility: Water solubility of the pollutant [mg/l]

Recharge: Is the description of the infiltration rate of water when entering soil. It is determined by the nature of type of precipitation or irrigation, the character of the soil, and the duration of the precipitation event.

Sorption Constant (K_d): The sorption constant, also called linear partition coefficient describes the relative distribution of the pollutant, partly sorbed by the solid phase and partly dissolved in the water. It is a site-specific value. A high value means by trend a great sorption to solid phase and a low value means a greater tendency of the pollutant to stay dissolved in water.

Solid-phase degradation rate constant (k_s): It includes the decay of the pollutant at the surface before it infiltrates into the soil. It is defined as rate of loss per hour and occurs by photodecomposition, volatilization and other processes.

Liquid-phase degradation rate constant (k_l): This parameter describes the processes which cause mass loss within the soil, primarily due to soil microorganisms but it can also depend on soil temperature and moisture.

Bulk Density (ρ_b): The bulk density is the mass of dry soil relative to the bulk of soil volume. [g/cm^3]

Saturated Water Content (θ_{sat}): This Parameter defines the volume of water relative to the bulk volume density at saturation. [cm^3/cm^3]

Charecteristic Curve Coefficient (b): Equation (8) describes the relation between relative saturation and relative conductivity of the soil under steady-state conditions. It is influenced by parameter *b* as follows:

$$\frac{K}{\mathrm{K_{sat}}} = \left(\frac{\theta}{\theta_{\mathrm{sat}}}\right)^{2\mathrm{b}+3} \qquad (8)$$

Saturated Hydraulic Conductivity (K_{sat}): To describe the rate at which water can move through soil at saturation, this parameter is used. Its units are given in [cm/hr]. To measure conductivity also density and kinematic viscosity of the water is considered, the standard conditions are defined at 15.6°C and for pure water.

Dispersion Coefficient (D): [cm^2/day] Despite considerably efforts to define this parameter, it is not fully understood and therefore difficult to distinguish. There exist empirical relationships generated by various experiments (Biggar and Nielson, 1976), but an evaluation via calibration of the model probably evaluates it the best.

Minimum x-value: [cm]. It defines the upper depth of the model domain. Normally this refers to the surface, which then has a value of 0.

Maximum x-value: [cm]: This criterion determines the lower depth, which in many cases is represented by the water table.

Minimum time value: The minimum time value describes the initial time boundary in days.

Maximum time value: This number describes the day of the end of simulation; it is the final time of interest.

Time values: This parameter defines the time value in which output is documented. Its unit is days.

Number of applications of waste: Number of applications prior to recharge in the simulation.

Waste application rate and starting time: This factor defines the mass of pollutant applied per hectare of land area (1 hectare [ha] equals 10 000 square meters [m^2]). The time interval between the application and the initiation of recharge is called the starting time. During this time the code simulates degradation. Under conservative conditions starting time is defined as 0. (Ravi and Johnson, 1982)

Output

The Pestan Program provides several output options including files that can be plotted as graphics. Pestan calculates data for three different types of graphs:

- Breakthrough curve
- Pollutant flux curve
- Soil-depth pollutant concentration profile

Additionally to the three types of graphic illustrations, the Pestan Model calculates some other results, like water and pollutant conditions:

- Projected water content, Pollutant [cm/hr]
- Pollutant velocity [cm/hr]
- Lenghth of pollutant slug [cm]
- Mass decayed prior to recharge [kg]

Also there are some calculations made concerning mass balance:

- Pollutant remaining in liquid-phase [kg]
- Pollutant remaining in solid-phase [kg]
- Total mass of pollutant remaining [kg]
- Liquid-phase decay of pollutant [kg]

And in addition a list of pollutant concentrations in relation to time and depth is included:

- Pollutant concentration in water (C_w [mg/l])
- Pollutant concentration in Soil (C_s [mg/kg])
- Total pollutant concentration (C_{tot} [mg/l])

(Ravi and Johnson, 1982, pp.19-22)

iv. Droplet

DROPLET is the acronym for "**DR**inkwater uit**OP**pervlaktewater **L**andbouwkundig gebruik**E**valuatie **T**ool". It enables Dutch Board for the Autorisation of Plant Protection Product and Biocides (Ctgb) to evaluate for the nine Dutch surface water abstraction points for drinking water production the expected pesticide concentration after Good Agricultural Practice. The drinking water standard was specified with 0.1µg/L, a level that should not be exceeded; otherwise purification by drinking water companies must be considered.

The overall calculation for this tool is called SWASH (**S**urface **WA**ter **S**cenario **H**elp). It controls models simulating runoff and erosion (PRZM), leaching the field drains (MARCO), spray drift calculations (internally in SWASH) and in the end water fate in the aquatic receiving aquatic systems like ponds, ditches and streams (TOXSWA). MACRO stands for macropore flow and is a Swedish model to calculate contribution of drainage to contaminant concentration level in the surface. SWASH and TOXSWA are described in detail below. In the DROPLET model the edge-of-field concentration in the FOCUS D3 ditch is used as a starting point for its calculation, for further details R.C. Leerdam et al. 2010 should be consulted.

Next, pesticides flow from the edge-of-field ditch to the abstraction points situated in larger water bodies downstream. On their way towards abstraction points, concentration of pesticides is diminished by pesticide dissipation processes and inflow from water that is free from pesticides. This reduction is estimated with the aid of intake area and pesticide specific factors as follows:

- the rate of the crop area with relevance and the whole intake area
- the market share of the pesticide
- the different timings of applications
- degradation and volatilization and sometimes
- additionally dilution by a lake or incoming river

(Leerdam et al., 2010)

v. Hair:

The HAIR (HArmonized environmental Indicators for pesticide Risk) instrument can calculate risk indicators in relation with the agricultural use of pesticides in European countries. The aim of HAIR is to calculate tendencies in aggregated risk for the environment as well as for human health posed by pesticides. It can be calculated at small scale (e.g. for a National Action Plan) in support of the evaluation of EU policies (Sustainable Use Directive EU 2009-128). (Kruijne et al., 2011, p.11).

There are now two versions existent (HAIR2010 and HAIR2014) with some changes in the newer version, like a separate database for geographical data. Version 2010 contains three databases: The Hair Database, which is obtained by Alterra. Alterra is part of the Wageningen UR (University & Research Center), an international expertise organization. From the Hair Database information about GIS Data (area, climate, soil), crop definitions, model parameter values, configuration and miscellaneous definitions are obtained. The other databases are about compounds and application records and should be maintained by the user. (Vlaming, Kruijne and Groenwold, 2011, p. 11)

The main software tool in the HAIR2010 package is responsible for the calculation of indicator values based cases that can be defined by the user himself. It is possible to define any number of cases in terms of underlying databases, period of analysis, area selection, compound selection and crop selection. Subsequently calculations of the indicator values are performed for the selected case and the results are saved. In addition with Hair an insight in the relation between compound properties, replacement of those values by the missing value routine and indicators that can be calculated in dependence on the availability of compound properties are given. (Vlaming, Kruijne and Groenwold, 2011, p.13)

There is a variety of risk indicators currently built in HAIR. It includes:

- aquatic indicators for algae, daphnia and fish
- a groundwater indicator
- terrestrial indicators for birds, mammals, earthworms and honey bees
- occupational risk indicators for operators, re-entry workers, bystanders and residents

(R. Kruijne et al., 2011, p.6)

The aquatic indicators for example express the risk potentially posed to aquatic ecosystems in a standard volume of surface water in a field ditch with standard water width and standard water depth by the pesticide use. The concentration of exposure is then compared to the toxicity data of for the aquatic example algae, daphnia and fish. For the groundwater indicator, exposure is compared with the drinking water criterion. (R. Kruijne et al, 2011, pp.13, 14)

The following figure is an example graph of the HAIR2010 software manual. It shows a result for Case 3, which is described in the manual as UK multiple applications. Its purpose is the exploration of usage database on regional basis from the UK, which has been delivered by the original Hair consortium in 2004. The area, the compound and the crop as well as the evaluation time can be selected. (Vlaming, Kruijne and Groenwold, 2011, p.57)

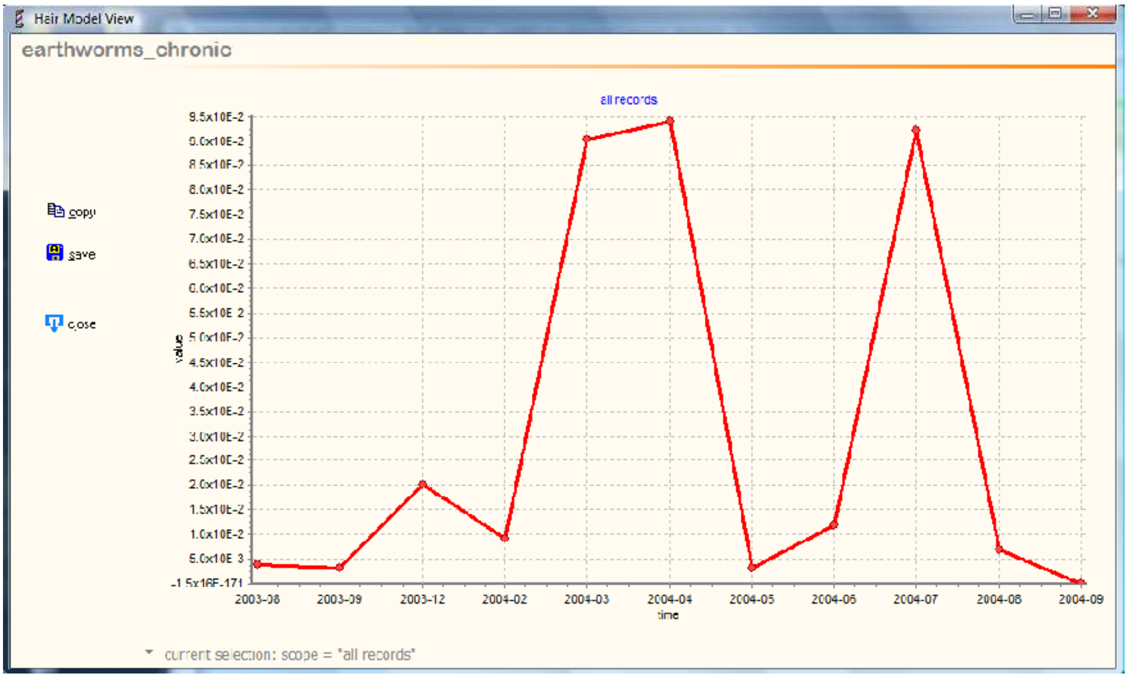


figure 13: Example of a result: earthworm chronic indicator in UK, time series (Vlaming, Kruijne and Groenwold, 2011, p.57)

The chronic risk indicator, which is illustrated by the figure, considers how a single or a multiple pesticide application within a growing season (crop cycle) effects on the growth and/or reproduction of earthworms (sublethal endpoint). It is calculated for the earthworms exposure for four weeks in the top five centimeter of the soil .The acute risk indicator in contrast looks at the effect a single or a multiple application of a pesticide within a single growing season (crop cycle) has on the survival of earthworms (lethal endpoint) after two weeks of exposure in the top five centimeter of the soil. (Kruijne et al., 2011, p.79)

For further details the HAIR2010 documentation or the software manuals for version 2010 or 2014 should be consulted.

vi. Pearl and GeoPEARL:

The use of the **PEARL** model is to evaluate leaching of pesticide to groundwater and in result should help in Dutch and European pesticide registration procedures. PEARL stands for **P**esticide **E**mmission **A**ssessment at **R**egional and **L**ocal scales. It was produced by *Alterra Green World research* and the *National Institute of Public Health and the Environment* (RIVM). It follow the models PESTLA and PESTRAS and since June 1st 2000 actually has replaced them. (Tiktak et al., 2000, p.3)

Besides its use as official tool in Dutch pesticide registration procedures it can also be applied at European scale, because it supports target quantities and scenarios set by the *Forum for International Co-ordination of pesticide fate models and their Use* (FOCUS).
(Tiktak et al., 2000, p.17)

PEARL is a one-dimensional, dynamic, multi-layer model. It gives a description of the fate of a pesticide as well as relevant transformation products in the soil-plant system. The *Soil Water Atmosphere Plant* (SWAP) model is an important factor in its hydrological calculations. There are mainly two different ways how pesticides can enter a system: either via direct application or by atmospheric deposition. The pesticide application methods available in this model are: spraying on the soil surface, spraying on the crop canopy, incorporation into the topsoil (for example by rototillage), and injection into the topsoil. In *figure 14* below the processes which are considered by the two models (PEARL and SWAP) are described.

They are: Transient state soil water flow, potential evapotranspiration, interception of water, water uptake by plant roots, evaporation of water from the soil surface, lateral discharge, heat flow, pesticide application, dissipation of pesticide from the crop canopy, convective and dispersive transport of pesticide in the liquid phase, diffusion of pesticide through the gas and liquid phases, equilibrium sorption and non-equilibrium sorption, first-order transformation kinetics, uptake of pesticide by plant roots, and volatilization of pesticide at the soil surface. (Tiktak et al., 2000, pp.23, 24)

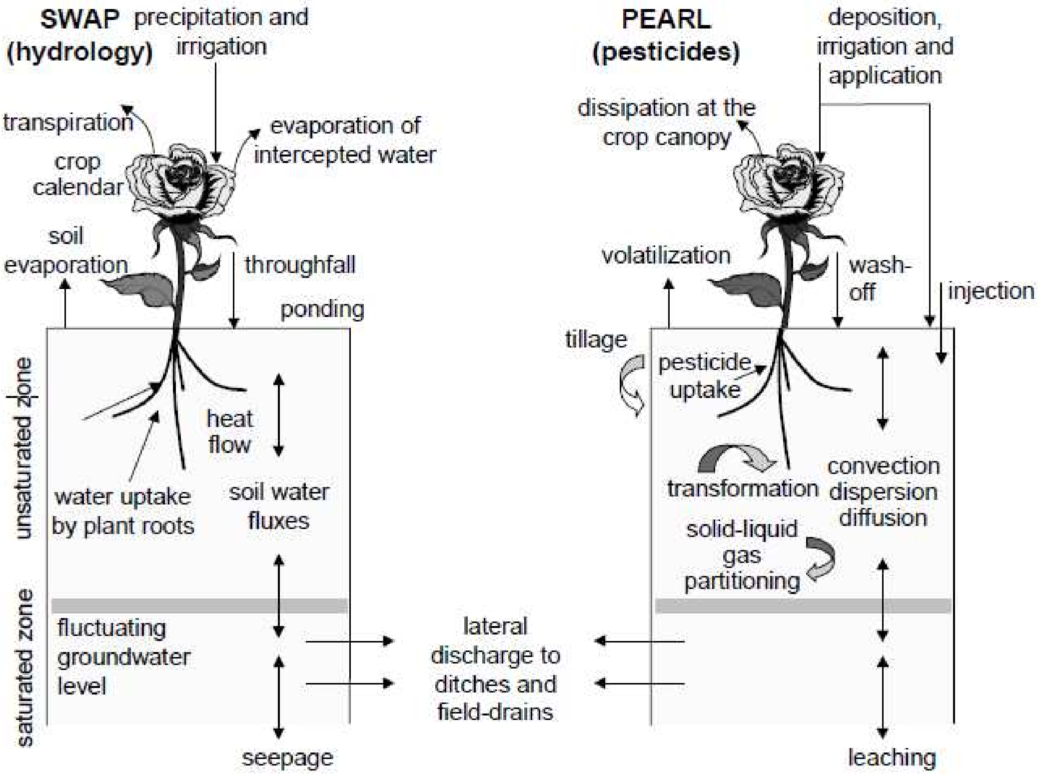


figure 14: Overview of processes included in PEARL and SWAP model (Tiktak et al., 2000, p.23)

There are a lot of ways how PEARL results can be illustrated. PEARL offers some predefined graphs (pesticide concentration in groundwater, areic pesticide mass etc.) but the user can also view the output data by defining graphs himself. (Tiktak et al., 2000, pp.106, 107)

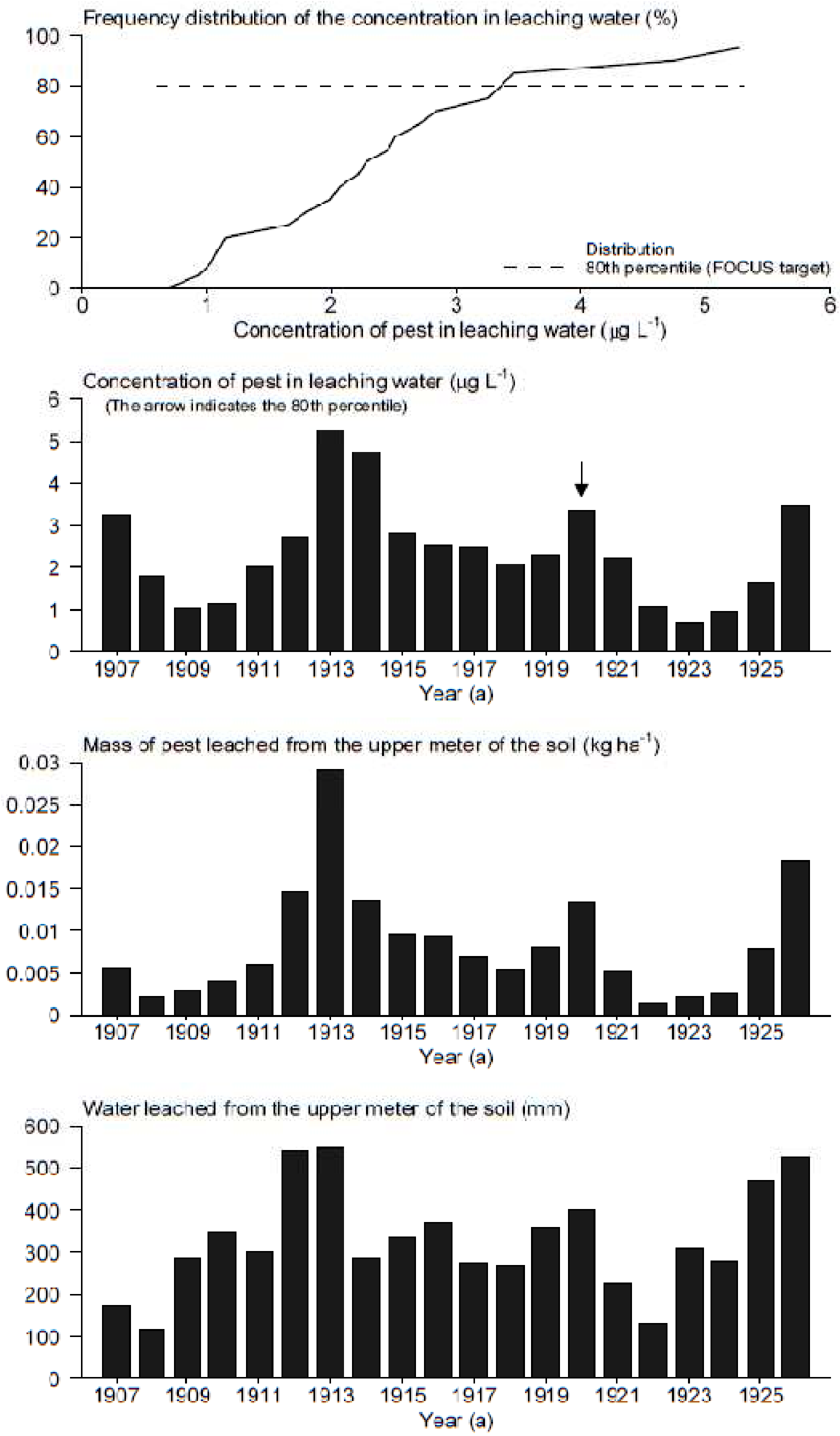


figure 15: example of a PEARL output: FOCUS summary graph (Tiktak et al., 2000, 108)

The figure above is an exemplary illustration of a predefined graph. The distribution of the concentration of the pesticide in the area of interest is shown, as well as the concentration and mass of the pest leaching from the soil.

The **GeoPEARL** model was also developed for evaluating leaching potential of pesticides, but with the specification to see if concentration in groundwater exceeds the EU drinking-water limit of a tenth microgram per liter (0.1 μg/L). The spatial criterion there states that in average over a longer period pesticide concentration or the one of its relevant metabolites should not exceed the drinking-water limit for at least ninety percent of the surface area in which the pesticide use is possible. (Tiktak et al., 2004, p.13)

GeoPEARL User Interface was developed by the PEARL team. This makes the access to data and model easy, consequently the structure of the database has much in common with the structure of the FOCUS PEARL database. (Tiktak et al. 2004, p.7)

Figure 16 shows an example result. It shows the class in the accumulated frequency distribution of the leaching concentration, so for instance fifty percent means that half of the soils are more vulnerable than the one of interest.

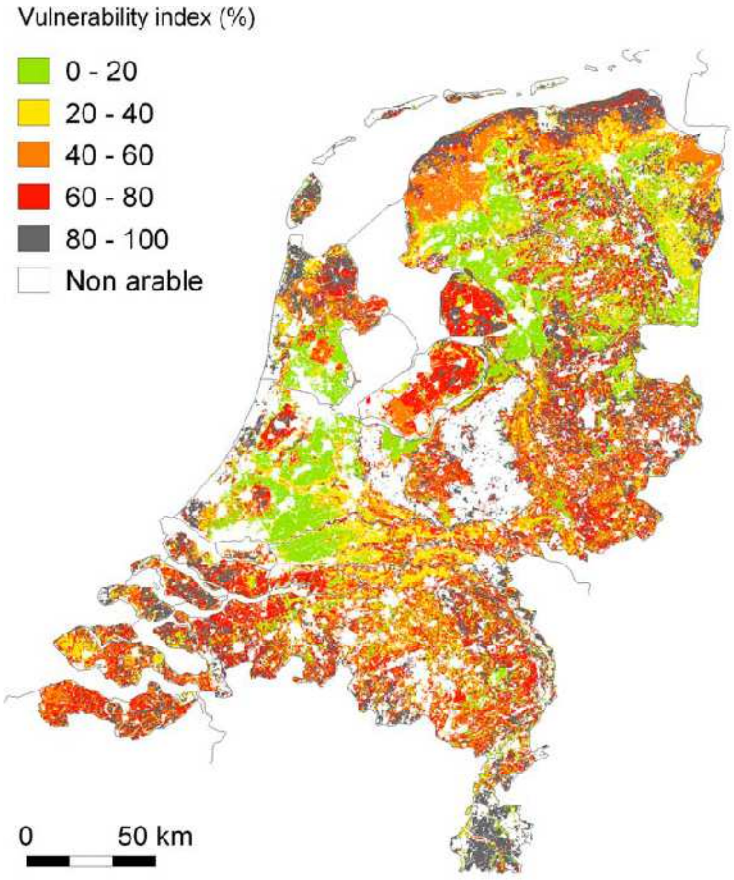


figure 16: Vulnerability of soils to the leaching of ordinary behaving pesticides (A. Tiktak et al., 2004, p.62)

vii. Perpest:

PERPEST model is able to **P**redicts the **E**cological **R**isks of **PEST**icides in freshwater ecosystems. In other words this system can in particular predict the effects of concentration of a pesticide on numerous (community) endpoints. In contrast to most of the other models PERPEST is based on empirical data extracted from the literature: The method used is called **Case-Based Reasoning** (CBR) and uses experience (e.g., published microcosm experiments) to solve new problems (e.g., what is the effect of pesticide A?). The database that contains the "past experience" is based on a review of freshwater model ecosystem studies, in which effects of pesticides have been evaluated. To apply these data on the question case, the PERPEST model searches for similar situations in the database, based on relevant characteristics of the compound like toxicity. Like this the model is able to predict effects of pesticides even if there has not been published any evaluation on a semi-field. The results of PERPEST are predictions showing the probability of effects, divided in classes (no, slight or clear effects, plus an optional indication of recovery), on the numerous grouped endpoints. (Nes and Brink, 2003, p.10)

The PERPEST model is especially helpful in cases of ecological risk assessment when there are a lot of uncertainties and not a lot of data available, for example if a new pesticide is tested. The results of PERPEST can give an idea of the direction in which uncertainties are likely to be large. So then in this direction data must be collected for a refined risk assessment (e.g. endpoints and exposure concentrations of interest). Another option for the output is the translation of spatially and temporal distributed concentration data into effect concentration, for example this data could be also used as a risk indicator. (Nes and Brink, 2003, p.13)

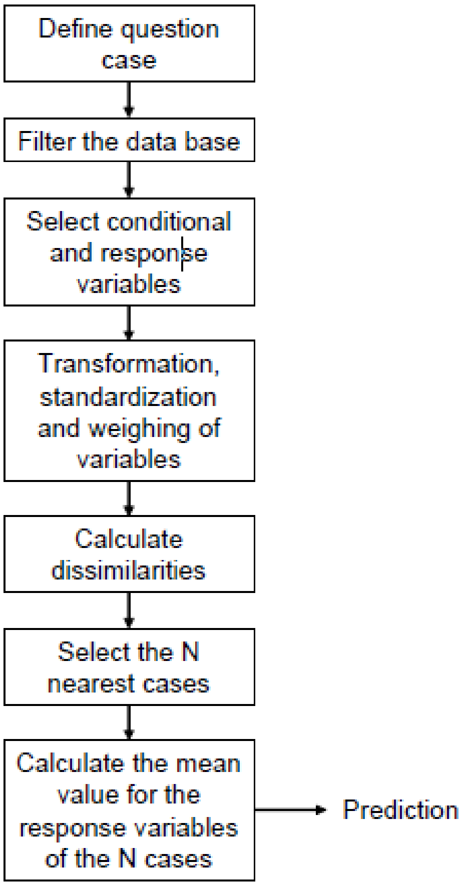
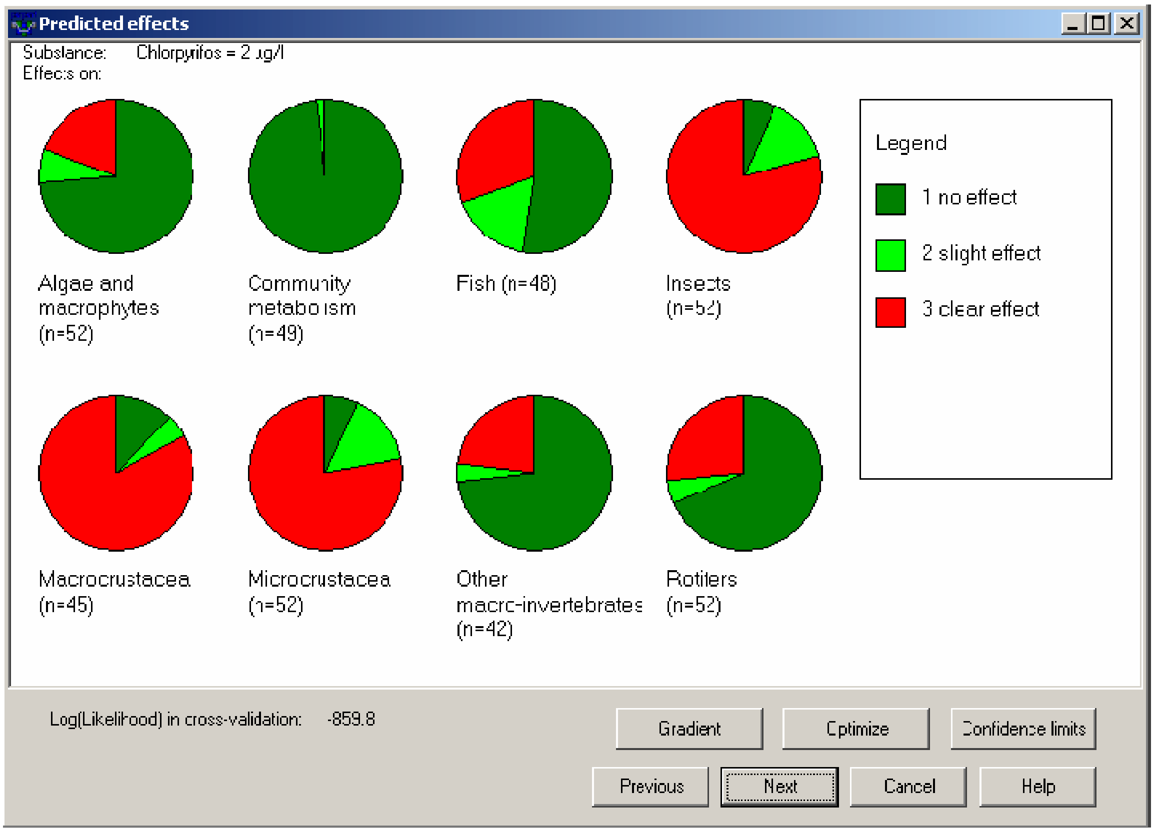


figure 17. Steps used in the CBR-method (Nes and Brink, 2003, p.19)

The figure on the side should illustrate the CBR-method that is used to predict the effects of a pesticide. The first step (defining question case) is to clear out the circumstance that should be predicted, e.g. name and concentration of the pesticide. Secondly the database is filtered on the basis of a logical equation (the result should be *True* or *False*, the result of comparison and logical functions like ><= *and or*). Then variables that should be used in the analysis are selected. Conditional variables (e.g. concentration of substance) and response variables (effect classes of herbicides or insecticides) are distinguished. Conditional variables in regression analysis are called independent variables and in the model they “explain” the effect of a substance. Response variables express the effect of a substance and in regression are called dependent variables. In the next step variables are transformed (e.g. by logarithmic transformation), afterwards the variables are standardized to give equal weight to different variables and then the variables can be weighted by the user himself and optimized by the computer. To calculate the dissimilarities between the question case and the other cases, a “dissimilarity index” is used. According to the obtained values the cases are ranked and the N nearest cases (default number: 25) are applied to make the prediction. (Nes and Brink, 2003, pp.19-21)

Figure 18 shows the screen of a summary of the results as pie charts. Each pie illustrates the predicted effect classes for that response variable. In this example the effects of chlorpyrifos, an insecticide which actually is also used for the application in this thesis, are shown. As seen it nearly has no effect on community metabolism but clearly affects macro- and microcrustacea as well as insects. (Nes and Brink, 2003, p.31)


Substance: Chlorpyrifos = 2 µg/l

Effects on:

Log(Likelihood) in cross-validation: -859.8

figure 18: example of predicted effects (Nes and Brink, 2003, p.31)

viii. Primet

The PRIMET Decision Support System (DSS) is developed to estimate the risk of pesticide use on the environment and human health via exposure, especially in developing countries. PRIMET is an acronym for **P**esticide **Ri**sks in the tropics to **E**nvironment, **M**an and **T**rade. There is only a minimum of input data needed. (Peeters et al., 2008, pp.4, 5)

This Primet DSS Version 2.0 is applicable for estimating risks of pesticide use to aquatic life, terrestrial life (earthworms), bees, no target arthopodes, the use of groundwater as drinking water and dietary exposure via the consumption of groundwater, vegetables, fish and macrophytes. The model works on risk assessment at the household level, which means that as input parameter for example data about pesticide application on a farmer's level is needed. (Peeters et al., 2008, p.12)

As a result risk assessment is expressed in *Exposure Toxicity Ratio's* (ETR). The ETR are determined through the division of the exposure by the safe concentration. An ETR smaller than 1 means exposure is lower than the 'safe' concentration and the risk is acceptable. But if the ETR is larger than 1 and smaller than a certain value (in this report 100), a risk is possible. In this case the use of higher tier risk assessment is recommended, therefore other models like PERPEST, TOXSWA or PEARL, which are also described in this chapter may be used. If ETR's are very large (e.g. higher than hundred) risks are very certain. However, it should be considered that the methods used are based on worst-case assumptions. (Peeters et al., 2008, p.14)

To run this program for risk assessment physical-chemical information as well as toxicity data of the active ingredient (e.g. toxicity, dissipation, and sorption) is necessary. Some of it is available in the PRIMET database. (Peeters et al., 2008 p.13)

Once all the input data is available risks are calculated for (edge of) field situations. These can be the ecology of water courses which are adjacent to the treated field, the terrestrial life within the treated soil, and invertebrates in and around plants. Also it can be calculated for human consumption of groundwater (e.g. as drinking water) near the treated field, human consumption of fish and macrophytes that live in the watercourse possibly affected by the pesticide use and also the human consumption of the cultivated crop itself.

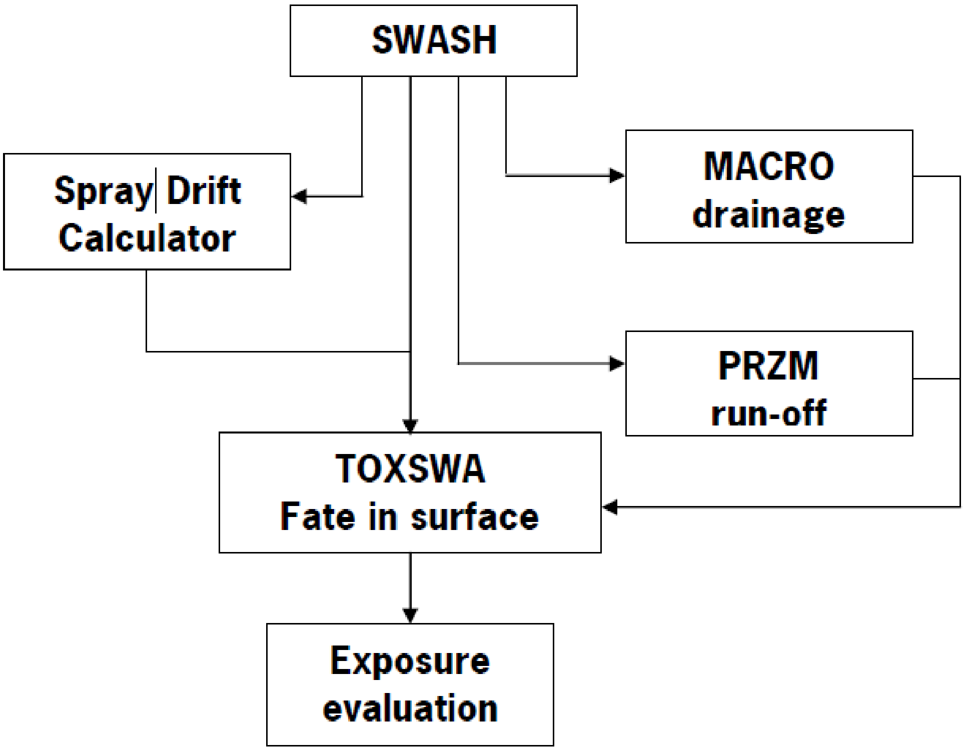
To make a risk assessment an evalutation for the exposure as well as for its effect has to be performed. In the first place the exposure assessment is made by estimating concentration of the compound in the area of interest (watercourses, terrestrial soil, groundwater, fish and macrophytes). Then the effect assessment is made, which consist in determining concentrations that are safe for the different compartments. This can be based on laboratory toxicity data, international standards or the use of extrapolation factor. To complete the risk assessment then the predicted concentration has to be divided by the estimated save concentration. (Peeters et al., 2008, p.14)

ix. Swash

SWASH stands for **S**urface **WA**ter **S**cenarios **H**elp. The three major routes through which pesticide can enter surface water are spray-drift, drainage and run-off. With the use of spray-drift deposition tables and the MACRO, PRZM and TOXSWA models assessment of exposure concentrations in surface waters is possible. These exposure scenarios are a development under the EU evaluation process conformable to 91/414/EEC (FOCUS, 2001). As illustrated in the figure below, to perform adequate exposure assessment scenarios for surface waters a drift assessment tool and two pesticide fate models are necessary and have to operate in correct order.

They have been developed separately as follows:

- Drift Calculator, calculating pesticide deposition due to spray drift
- FOCUS_PRZM_SW_1.1.1, calculating pesticide entry into surface water through run-off
- FOCUS_MACRO_4.4.2, calculating pesticide entry into surface water through drainage
- FOCUS_TOXSWA_2.2.1, calculating the fate of pesticides in surface waters.



ce Water Scenarios

In all FOCUS Surface Water Scenarios developed there was made the assumption that pesticides only enter water in the surface via two pathways. This means surface water can be either contaminated due to deposition of the pesticide caused by spray drift plus drainage or due to pesticide deposition caused by spray drift in combination with runoff.

The MACRO model (Jarvis, 1994; Jarvis & Larsson, 1998) enables to make an estimation of the behavior of pesticides in soils with and without macro-pores. In this model transport by convection and diffusion through liquid phase, sorption and transformation are considered. The version included in FOCUS_MACRO version 4.4.2 contains some improved process descriptions (e.g. snow pack, Freundlich sorption). Additionally when the simulation run of a compound has ended it is able to simulate transport, fate and general behavior of one metabolite of this “parent compound” in soil.

The PRZM model (Carsel et al., 1998) on the other hand makes the simulation of the movement of chemicals within and immediately below the root zone of unsaturated soils possible. It is a one-dimensional model. The use of it in the FOCUS model is to determine run-off and soil erosion into surface water. The USDA Soil Conservation Service curve number methodology and several variations of the Universal Soil Loss Equation are basis for its calculation. With PRZM in FOCUS version three transformation schemes and up to two metabolites (a parent with one metabolite, a parent with 2 sequential metabolites and a parent with 2 metabolites) can be determined.

To describe pesticide behavior in small water bodies, TOXSWA model is used. The processes that this model considers are sorption, transport, volatilization and transformation.
As an overview of all Step 3 FOCUS runs for a specific case, for the calculation of the spray drift deposition onto various receiving water bodies, to maintain a basic pesticide properties database and for the preparation of all inputs needed for the other models the SWASH program was developed. It can be seen as an overall shell, managing the communication and data transfer between the models considered in the calculations.
(Berg et al., 2008, pp.9-12)

x. TOXSWA

In the TOXSWA behavior of pesticides in a water layer and its underlying sediment at the edge-of-field-scale is described. TOXSWA stands for **TOX**ic substances in **S**urface **WA**ters. In Netherlands in 1999 and in Europe with FOCUS_TOXSWA in 2003 TOXSWA model was adapted for the calculation of Predicted Environmental Concentrations in surface water to support procedures of pesticide registration.

TOXSWA v1.2, a simulation in constant water depths and discharges is made. For the FOCUS_TOXSWA some more hydrological investigations and developments have been made. It is possible that surface runoff from a small upstream catchment basin and water of a field next to pesticide treatment as well as pesticide fluxes from drainage rush into a ditch or small stream. With FOCUS_TOXSWA the simulation of the resulting transient flow regime can be made. The discharges and water levels in the ditch or small stream can be rapidly varying. As explained before for the use in the EU registration procedure FOCUS_TOXSWA is coupled to the MACRO and PRZM models to simulate exposure concentrations in the FOCUS Surface Water Scenarios. (PesticideModels.eu Toxswa Home, 2015)

The TOXSWA model is able to predict concentrations of pesticides with possible entrance processes into the water like spray drift, atmospheric deposition, surface runoff, drainage or leaching through the soil. (PesticideModels.eu Toxswa Documentation, 2015)

In the model the following processes are considered: transport, transformation, sorption and volatilization of pesticides. By definition the water layer includes suspended solids and aquatic macrophytes. The characteristics for the sediment layer are porosity, organic matter content and bulk density that vary with depth. It must be said that sedimentation and resuspension of suspended solids are not taken into account. (PesticideModels.eu Toxswa Documentation, 2015)

Advection and dispersion dominate the transport of pesticides in the water layer. In the sediment, additionally diffusion has to be considered. Concerning transformation its dependence on temperature has to be considered. The combination of the effects of hydrolysis, photolysis and biodegradation is covered by the transformation rate. For the determination of sorption to suspended solids as well as to the sediment itself the nonlinear Freundlich equation, which was been discussed more detailed in chapter *ii. Pestan,* is used. For the description of sorption to macrophytes a linear isotherm is used. The transport of pesticides across the water-sediment interface can take place via upward or downward seepage and via diffusion. The resolution variety can be one hour to one day concerning temporal resolution or about hundred to two thousand meter talking about the watercourse length. The thickness of the sediment is about 10 centimeter. (PesticideModels.eu Toxswa Documentation, 2015)

In the following two figures, two of the FOCUS scenarios are illustrated in scheme:

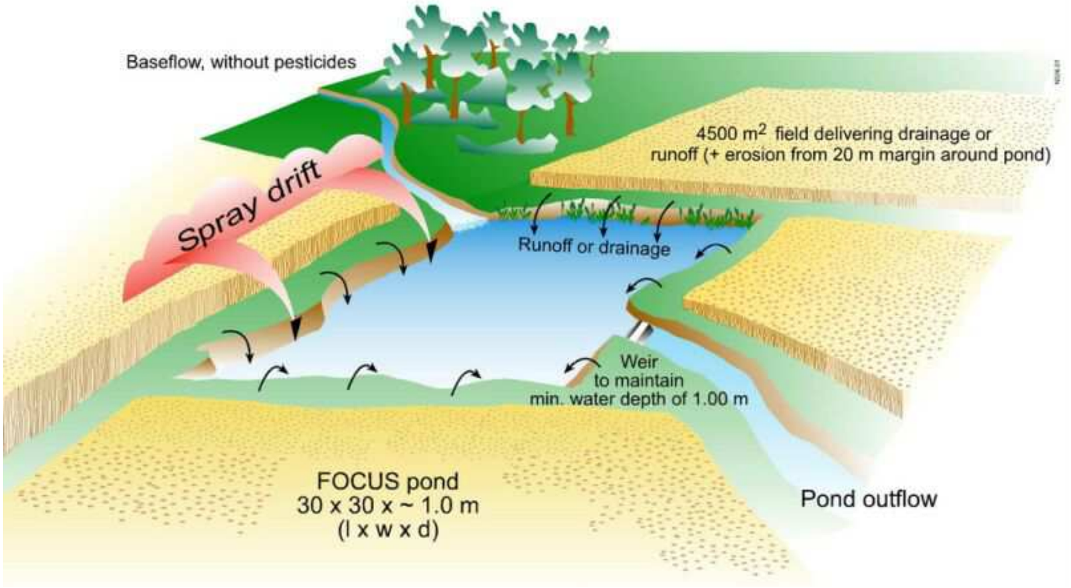


figure 20: Focus pond scenario (PesticideModels.eu Toxswa EU-Registration, 2015)

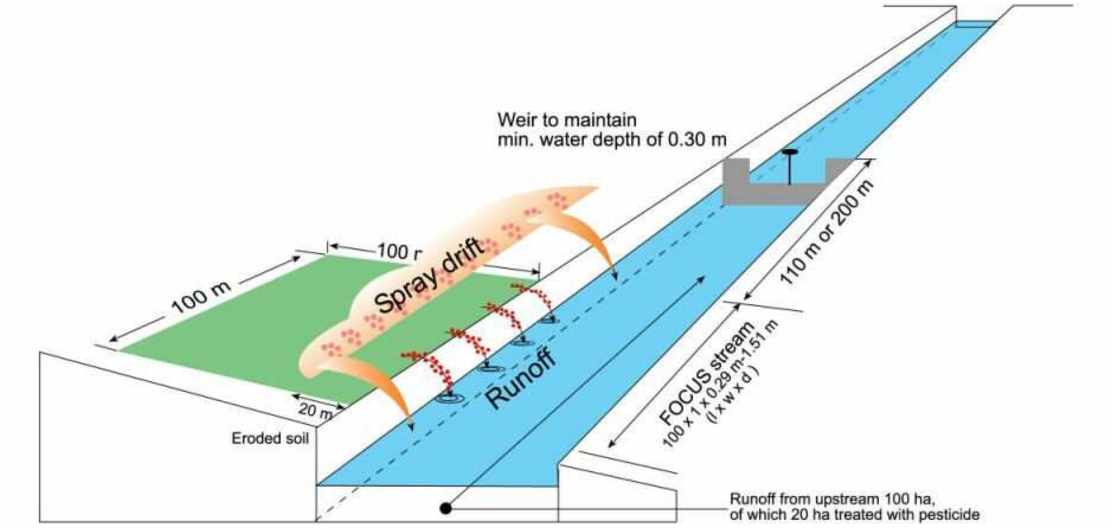


figure 21: Focus stream scenario (PesticideModels.eu Toxswa EU-Registration, 2015)

iii. Cascade:

CASCADE is a program to assess exposure concentrations of plant protection products in small water-channel-systems with the basis of good agricultural practice of these products. Typically it is applied for area of interest of the order of ten square meters.

The CASCADE software tool has the following components:

Firstly there is the CASCADE_Drift Model, which calculates the amount of spray drift on the water surface of the pilot region. The results are essential supplies for the input of pesticides into the water system. There are many parameters integrated which can be adjusted by the user. Weather conditions (relative humidity, wind velocity and direction, air temperature) can be determined by using general data of the pilot region or by adapting the data manually. It is possible to select the spray technique as well as the day and the time when the different fields are sprayed.

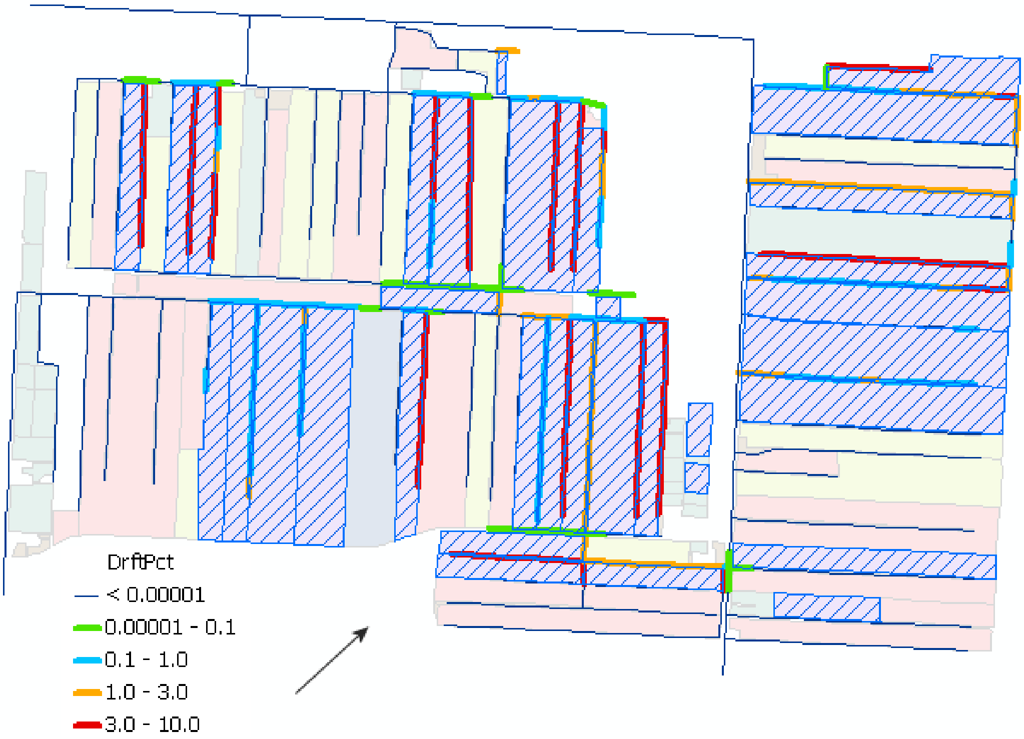


figure 22: example of an resulting graph of calculations by CASCADE_drift (PesticideModels.eu Cascade, 2015)

The figure above shows the distribution of the spray drift deposit on the pilot region (potato fields) on the website. The hatched areas are the areas where spray drift is applied. The arrow shows the average wind direction and the thick colored lines are the ones that receive spray drift.

After that the data is put into CASCADE_TOXSWA-Model to calculate exposure concentrations in water. The fate of pesticides can be estimated. The figure bellow shows the result of the program of one day. The x-axis describes the distance from the upstream end of the watercourse. In the upper bar, black vertical lines can be seen. They represent junctions of water courses. If contaminated water joins water without contaminant it dilutes and concentration may drop rapidly across a junction. (PesticideModels.eu Cascade, 2015)

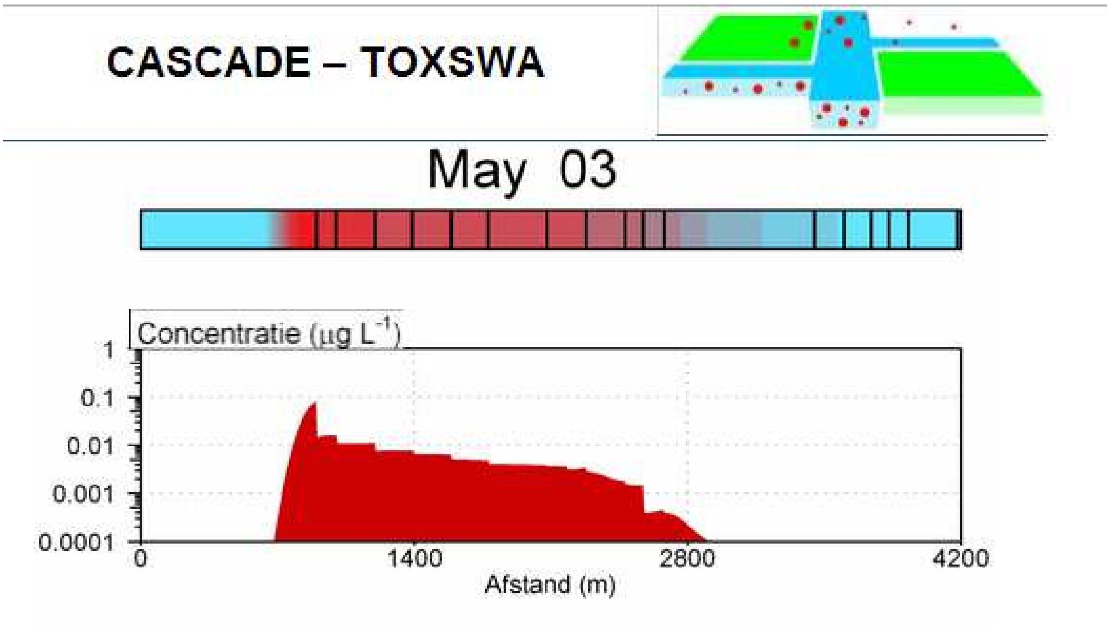


figure 23: Output of the Cascade-Toxswa-Model (PesticideModels.eu Cascade, 2015)

5. Application to a synthetic case based on real data

a) Pesticide Chlorpyrifos:

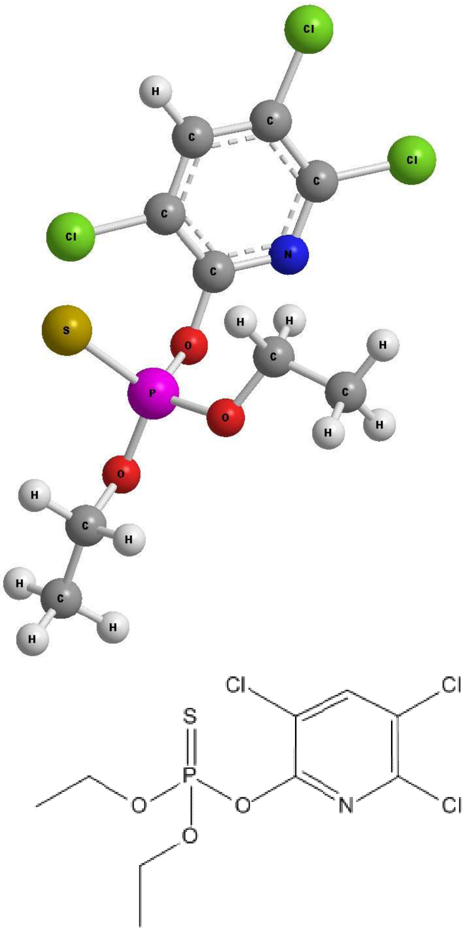


figure 24: Molecular structure – Chlorpyrifos (Christensen et al., 2009, p.1)

The chemically correct name for Chlorpyrifos is 0,0-diethyl 0-(3,5,6-trichloro-2-pyridinyl-phosphorothioate. It is classified as a chlorinated organophosphate and is used as insecticide, acaricide and nematicide. In the graphic on the right side the molecular structure of Chlorpyrifos is illustrated.

Uses:

Chlorpyrifos is applied on agricultural food and feed crops. Additionally it is used on cattle ear tags, golf course turf, industrial plants and vehicles, non-structural wood treatments including processed wood products, fence posts and utility poles. Also it can be used for the control of public health pests such as mosquitoes and fire ants.

Chlorpyrifos is said to be a non-systemic insecticide. It should be effective by direct contact, ingestion, and inhalation. (Christensen et al., 2009, p.1)

Due to the same technical fact sheet Chlorpyrifos is a colorless to white crystalline solid. Its smell is mildly mercaptan (thiol), which is described to be similar to the odor of sulfur compounds that can be found in rotten eggs, onions, garlic and skunks. Also some other physical and chemical properties are listed there, for example:

- Vapor pressure: 1.87 x 10^{-5} mmHg at 25°C
- Octanol-Water Partition Coefficient (log K_{ow})2: 4.70
- Henry's constant: reported values: 2 x 10^{-6} atm*m^3/mol at 25°C and 6.7 x 10^{-6}atm*m^3/mol (depending on the technique used)
- Molecular weight1: 350.6 g/mol
- Solubility (water): 0.0014 g/L (1.4 mg/L) at 25°C
- Soil Sorption Coefficient (K_{oc}): 360 to 31,000 depending on soil type and environmental conditions (Christensen et al., 2009, p.1)

b) Input Data: Pesticide Chlorpyrifos

Water Solubility: For the Water Solubility different values can be found: In the PESTAN Guide in Appendix A "Properties of selected pesticides" water solubility of Chlorpyrifos is stated to be 2 [mg/L] at 25°C. (Ravi and Johnson, 1982, p.A-1) Due to Christensen et al., 2009, p.1 Solubility in water is given as 0.0014 [g/L], 1.4 [mg/L] at a temperature of 25°C. Also in the technical inform of Dorkasa Perú about Extrafos (common name: Chlorpyrifos) the water solubility is given with 1.4 [mg/L] at 25°C. (Dorkasa Perú, 2015) Due to this different values for this application Chlorpyrifos water solubility is estimated to be **1.4 [mg/L] at 25°C**.

Recharge: Due to Ilarri, 2010, p.24 the precipitation in the plain of Valencia can be estimated with about 450mm/yr. Irregular variations were measured over the year with maximal precipitation in autumn and spring and minimal values in summer. The average temperature is given with 10°C in winter and 25°C in warm and dry summers where maximal temperature can be over 30°C. As an assumption, ignoring probable additions due to irrigation a recharge of **450 [mm/yr] = 0.00514 [cm/hr]**.

Sorption Constant (K_d): As explained in the PESTAN Guide the sorption constant K_d can be calculated approximately with the following equation:

$$K_d = K_{oc} * f_{oc} \quad (9)$$

where
f_{oc} =... fraction organic carbon content of the soil
K_{oc} =...organic carbon partition coefficient [L/kg]
(Ravi and Johnson, 1982, pp. 15, 16)

There can be found reference value for different types of soil in PESTAN Guide, for example **0.61 for loamy sand or 0.72 for sandy loam** as values for percent of organic matter (f_{om}). (Ravi and Johnson, 1982, p. B-1) This value has to be divided by 1.724 to calculate the organic carbon content (f_{oc}) (EPA, c.1994, p.8), but is actually directly used a reference value for the f_{oc} in the PESTAN program. The transformation from the f_{om} to f_{oc} is not being calculated when using the PESTAN program. As this paper is an analysis of the PESTAN program we also use the not transformed f_{om} value directly as f_{oc}. The soil of the plain of Valencia, especially the zone around Aldaia, can generally be assumed to be characterized

by sandy loam or loamy sand. (Ilarri, 2010, pp. 19, 49-53) The sensitivity of the PESTAN program to this apparently marginal difference will be analysed later.
For the Organic carbon partition coefficient (K_{oc}) values can range between 360 and 31000. This indicates that the chemical is not very mobil as it is sorbed strongly to suspended solids and sediments. (Smegal, 2000, p.19) In this case the lowest value is chosen (**360[L/kg]**), as the water table is estimated to be very low (55m) it is interesting to estimate the time it will take at least until the contaminant reaches this level. However this means that persistence in dependence on this value is assumed to be minimal.

Solid-phase degradation rate constant (k_s): Due to Ravi and Johnson (1982, p.29) in the PESTAN Guide and also Brusseau and Chorover (2006, p.103) the solid-phase degradation rate constant (k_s) can be estimated depending on half life as seen in equation (10). Half life ($T_{1/2}$) of Chlorpyrifos at the air is estimated to be four to eleven hours (Christensen et al., 2009, p.11).

$$k_s = \frac{0.693}{T_{1/2}} \qquad (10)$$

=0.693/$T_{1/2}$=0.693/11=**0.063**=k_s [rate/hr]

Liquid-phase degradation rate constant (k_l): The liquid phase degradation rate can be calculated with the same equation (10). Half life in soil is estimated to count between eleven and one hundred and eighty days and a mean of 28.7. (Smegal, 2000, p.19)

=0.693/(28.7*24)=**0.001**=k_l [rate/hr]

Bulk Density (ρ_b): Value of the PESTAN Reference Soil Types: 1.335 [g/cm^3] for Sandy Loam; 1.62 [g/cm^3] Laomy Sand as given by the program

Saturated Water Content (θ_{sat}): In the PESTAN Guide there can be found values for different types of soil: 0.41 [cm^3/cm^3] for loamy sand and 0.423-0.435 [cm^3/cm^3] for sandy loam. (Ravi and Johnson, 1982, p. B-1) In this application a value of 0.435 is used by the program as reference value for sandy loam.

Characteristic Curve Coefficient (b): In the same paper the characteristic curve coefficient (b) is estimated depending in soil texture: 4.38 for loamy sand and 4.90 for sandy loam. (Ravi and Johnson, 1982, p. B-2)

Saturated Hydraulic Conductivity (K_{sat}): Also for the Saturated Hydraulic Conductivity (K_{sat}) reference values can be found in the PESTAN Guide. For loamy sand it is estimated to be between 56.28 and 78.84 [cm/hr], for sandy loam between 12.48 and 17.93 [cm/hr]. (Ravi and Johnson, 1982, p. B-2). Using the reference soil types of the PESTAN program, however, values are used that are relatively different. For sandy loam a K_{sat} of 4.42 [cm/hr] is used and for loamy sand a value of 14.59 [cm/hr]. For this thesis the last two values are chosen.

Dispersion Coefficient (D): As explained in the PESTAN Guide this value is very difficult to determine. For this reason It is assumed to be the same as in the PESTAN sample: 0.06 [cm^2/day]. In the sample this value is determined for sandy soil. (Ravi and Johnson, 1982, p. 30)

Minimum x-value: 0 [cm]

Maximum x-value: In the PESTAN sample a value of 200 [cm] is chosen (Ravi and Johnson, 1982, p. 30); data for the pond in Aldaia indicates a water table of 5500 [cm] (Ilarri, 2010, p. 54). In this case we apply a maximum x-value of 500 [cm], with variations for some examples.

Minimum time value: 0

Maximum time value: 1000 (varies)

Time values: mostly 50, 100, 150, 200, 365, 5000 (Days)

Number of applications of waste: 1

Waste application rate and starting time: The general amount of application in the plain of Valencia is estimated to be around 2[kg/ha]. To analyze the sensitivity of the PESTAN program to waste application changes and its general influence on fate of the contaminant in the environment we apply in one case an amount increased with fifty percent and on decrease with fifty percent.

c) CASE 1: Sandy Loam; waste application rate: 2 [kg/ha]

Water Solubility: 1.4 [mg/L] at 25°C.

Recharge: 450 [mm/yr] = 0.00514 [cm/hr].

Sorption Constant (K_d): f_{om} = 0.0071 for sandy loam, K_{oc}=360 [L/kg] → K_d=2.556

Solid-phase degradation rate constant (k_s): 0.063 [rate/hr]

Liquid-phase degradation rate constant (k_l): 0.001 [rate/hr]

Bulk Density (ρ_b): 1.335 [g/cm^3]

Saturated Water Content (θ_{sat}): 0.435 [cm^3/cm^3] for sandy loam

Characteristic Curve Coefficient (b): 4.90 for sandy loam

Saturated Hydraulic Conductivity (K_{sat}): 4.42 [cm/hr] for sandy loam

Dispersion Coefficient (D): 0.06 [cm^2/day]

Minimum x-value: 0 [cm]

Maximum x-value: 500 [cm] (varies)

Minimum time value: 0 [days]

Maximum time value: 8000 [days] (varies)

Time values: 50 [days]

Number of applications of waste: 1

Waste application rate and starting time: 2 [kg/ha]

As the following two figures show, with PESTAN it can be shown in a simple way how the flux of contaminant evolves with the depth. In this case whilst it takes about one thousand one hundred days at a depth of 50 cm until the peak of the concentration curve with about 14 ppb arrives, it takes the same peak about four thousand six hundred days to arrive at a depth of 200 cm with a lower concentration of less than 0.01 ppb as maximum.

The same fate can be seen in the two figures (*figure 27 & 28*) later, which show the Leachate Total Mass Flux at the same depths (50 cm and 200 cm). There the flux is illustrated in total mass [kg] and the Total Mass In, Total Mass Out and Total Mass Remaining can be examined.

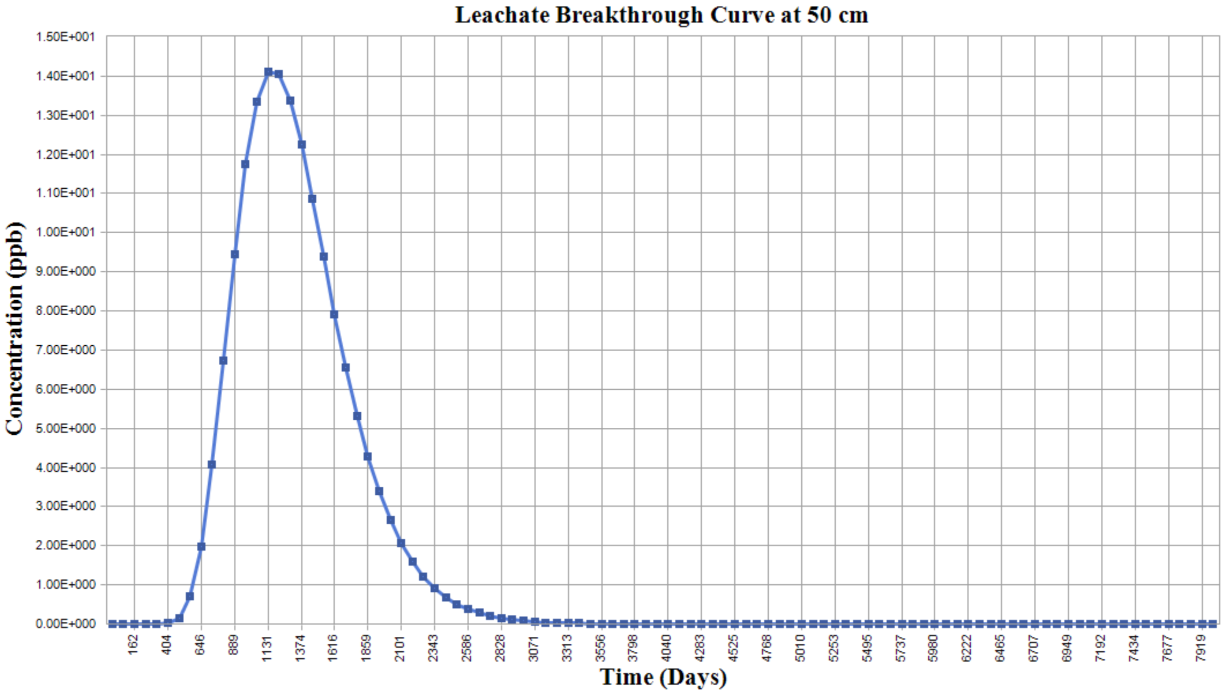


figure 25: Case 1: Leachate Breakthrough Curve at 50 cm

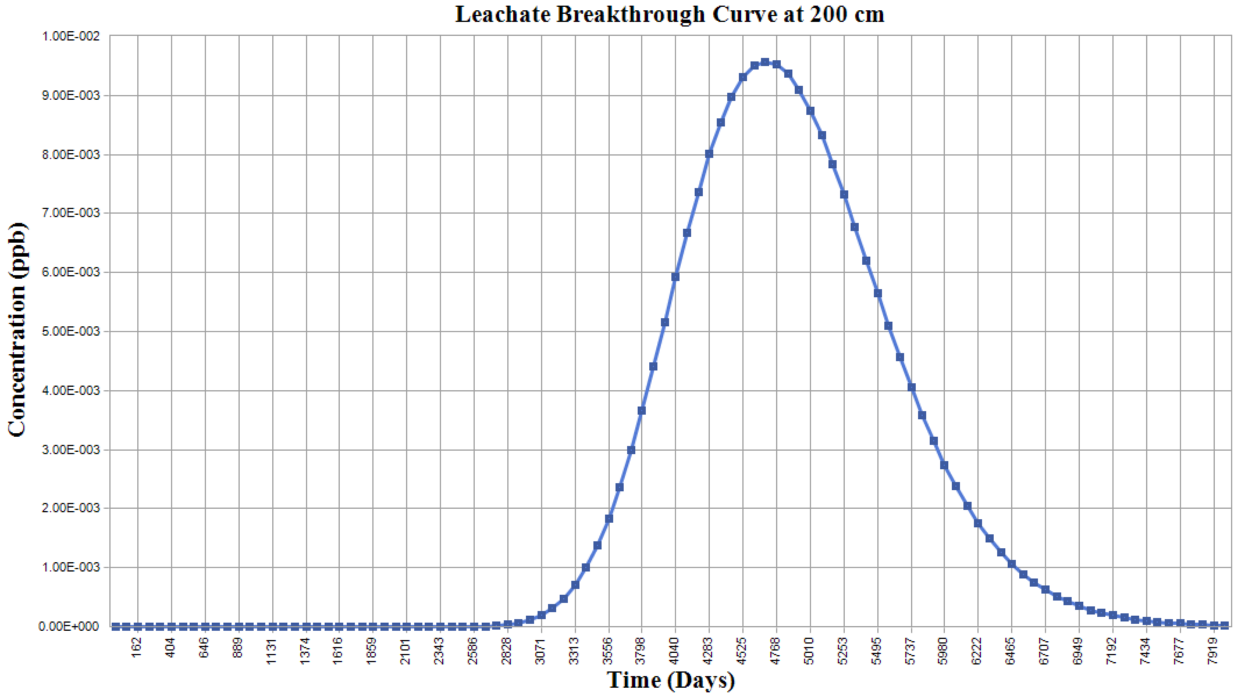


figure 26. Case 1: Leachate Breakthough Curve at 200 cm

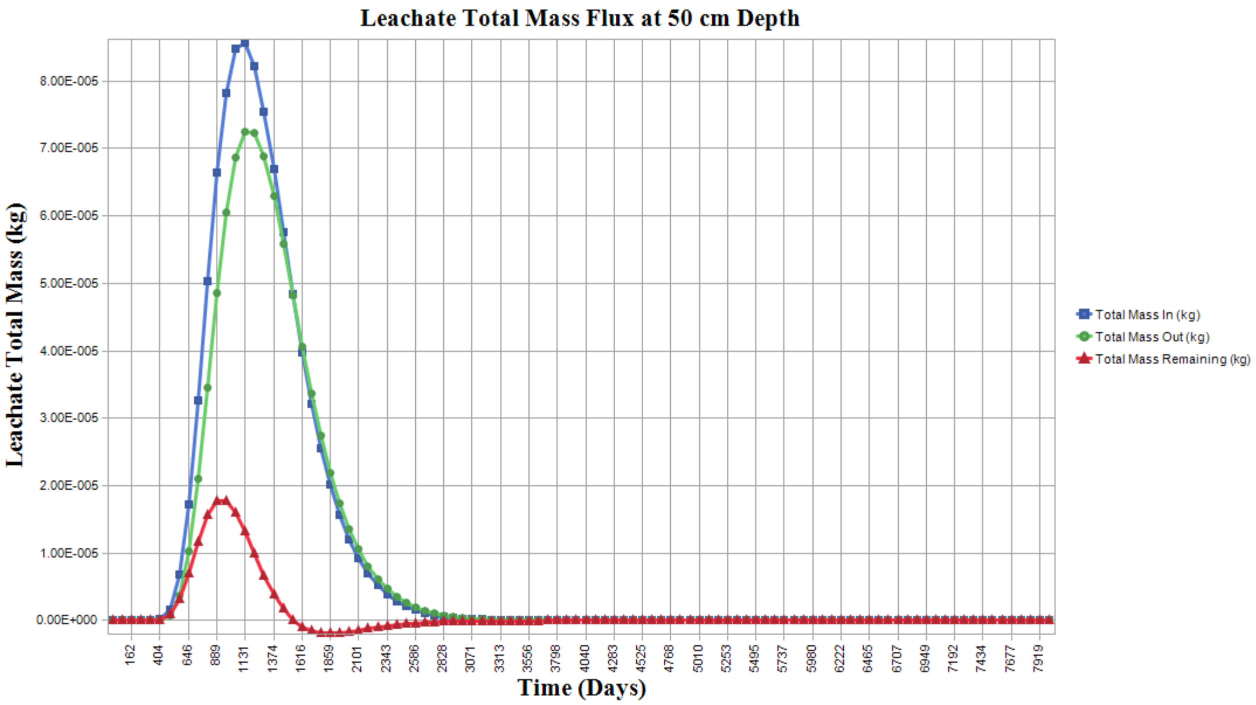


figure 27: Case 1: Leachate Total Mass Flux at 50 cm Depth

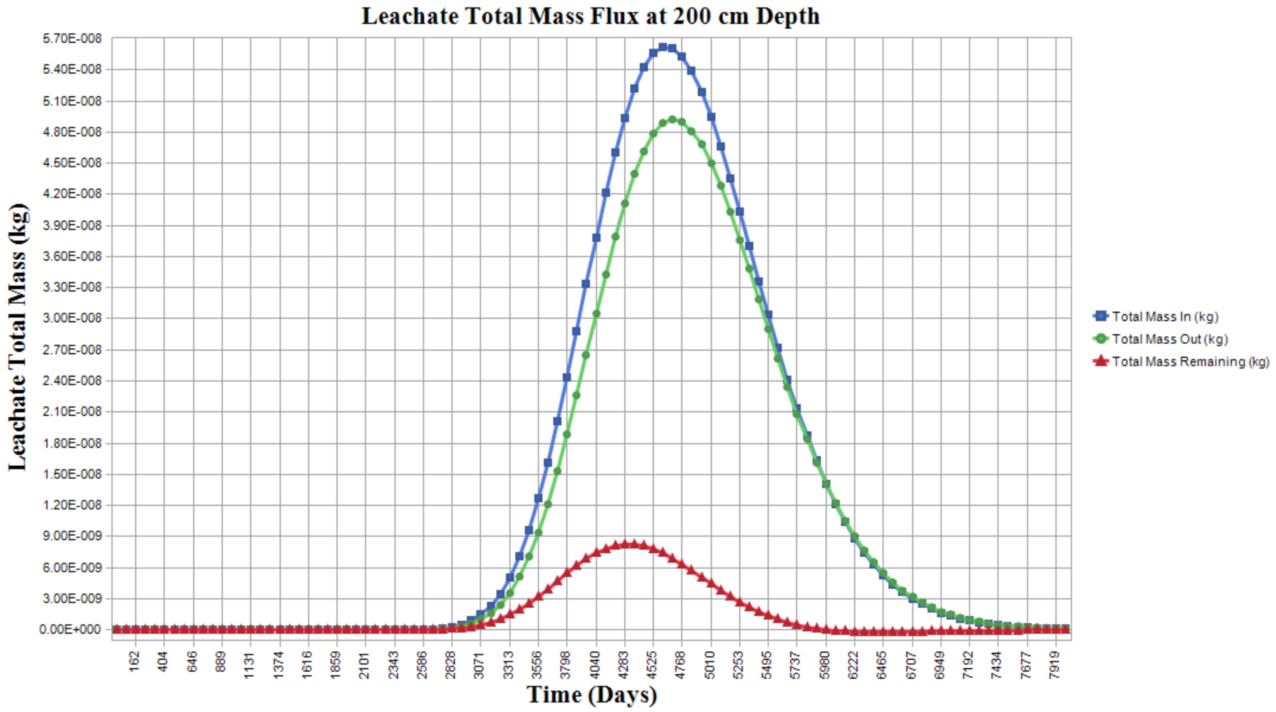


figure 28: Case 1: Leachate Total Mass Flux at 200 cm Depth

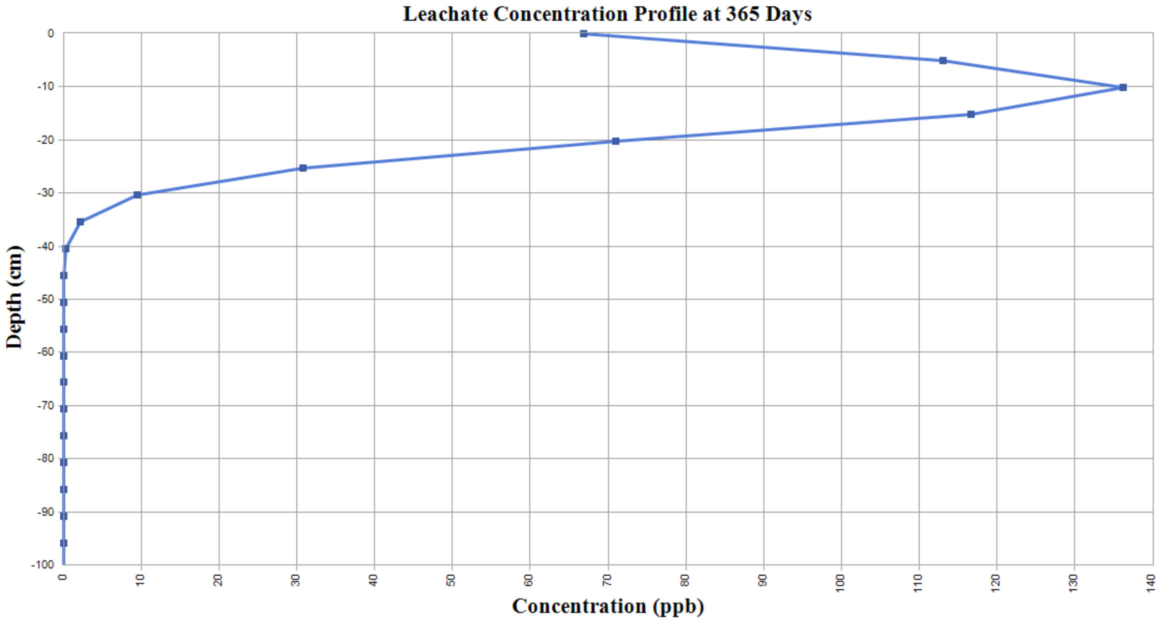


figure 29: Case 1: Leachate Concentration Profile at 365 Days

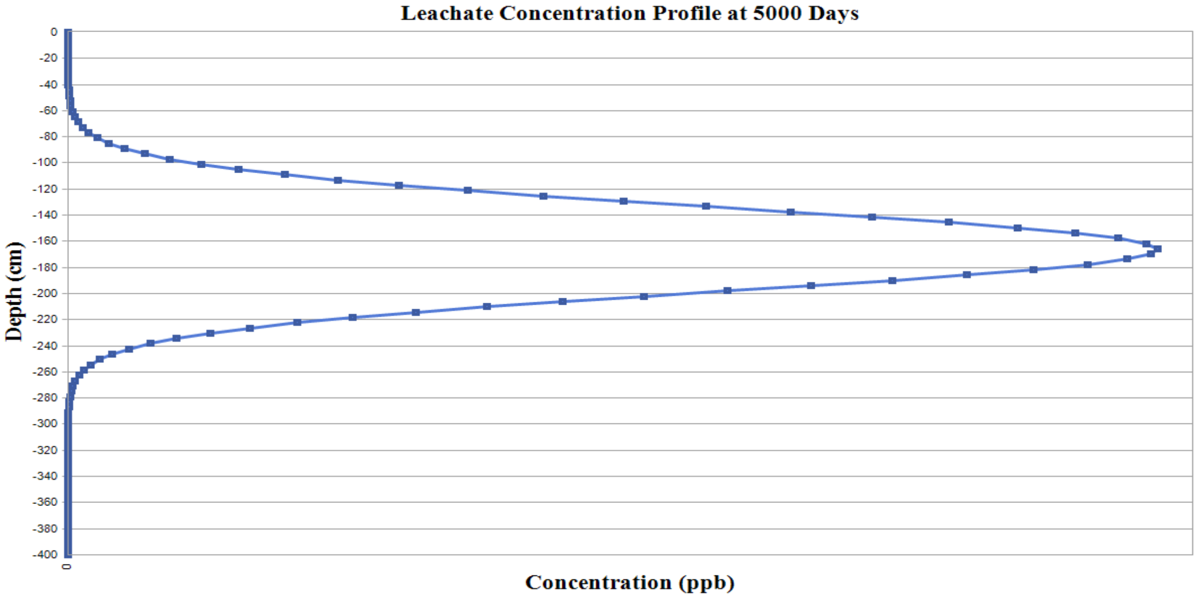


figure 30: Case 1: Leachate Concentration Profile at 5000 Days

In the two figures above the transport of the Leachate Concentration Profile can be observered. In the case of Chlorpyrifos, after one year (365 Days) at a depth of 10 cm the contaminant is still present with a concentration of up to 135 ppb, but do yet not reach depth levels of more than 40 cm. After thirteen and a half year (5000 Days) the peaks of the contaminant concentration is at about 170 cm depth, the concentration itself is already very low with a maximum of about 1.55E-02.

d) CASE 2: Sandy Loam; decreased waste application rate: 1 [kg/ha]

Water Solubility: 1.4 [mg/L] at 25°C.

Recharge: 450 [mm/yr] = 0.00514 [cm/hr].

Sorption Constant (K_d): f_{om} = 0.0071 for sandy loam, K_{oc}=360 [L/kg] → K_d=2.556

Solid-phase degradation rate constant (k_s): 0.063 [rate/hr]

Liquid-phase degradation rate constant (k_l): 0.001 [rate/hr]

Bulk Density (ρ_b): 1.8 [g/cm^3]

Saturated Water Content (θ_{sat}): mean of 0.435 [cm^3/cm^3] for sandy loam

Characteristic Curve Coefficient (b): 4.90 for sandy loam

Saturated Hydraulic Conductivity (K_{sat}): mean: 4.42 [cm/hr] for sandy loam

Dispersion Coefficient (D): 0.06 [cm^2/day]

Minimum x-value: 0 [cm]

Maximum x-value: 500 [cm] (varies)

Minimum time value: 0 [days]

Maximum time value: 1000 [days] (varies)

Time values: 50 [days]

Number of applications of waste: 1

Waste application rate and starting time: 1 [kg/ha]

Subsequently three graphs are shown; they illustrate the Leachate Concentration Profile two hundred days, one year and after nearly fourteen year (5000 Days). In comparison to the analog figure in Case 1, where the application of 2 [kg/ha] is simulated, the maximal concentration of the Leachate Concentration Profile, although at the same depth of about 170 cm is very low: about 7.75E-03 ppb compared to about 1.55E-02 in Case 1.

Observing the second figure it can be seen how with the time the maximum concentration moves deeper with decreasing concentration. One year (365 Days) after the beginning of the application the concentration maximum of about 68 ppb is estimated to be located at a depth of around 12 cm.

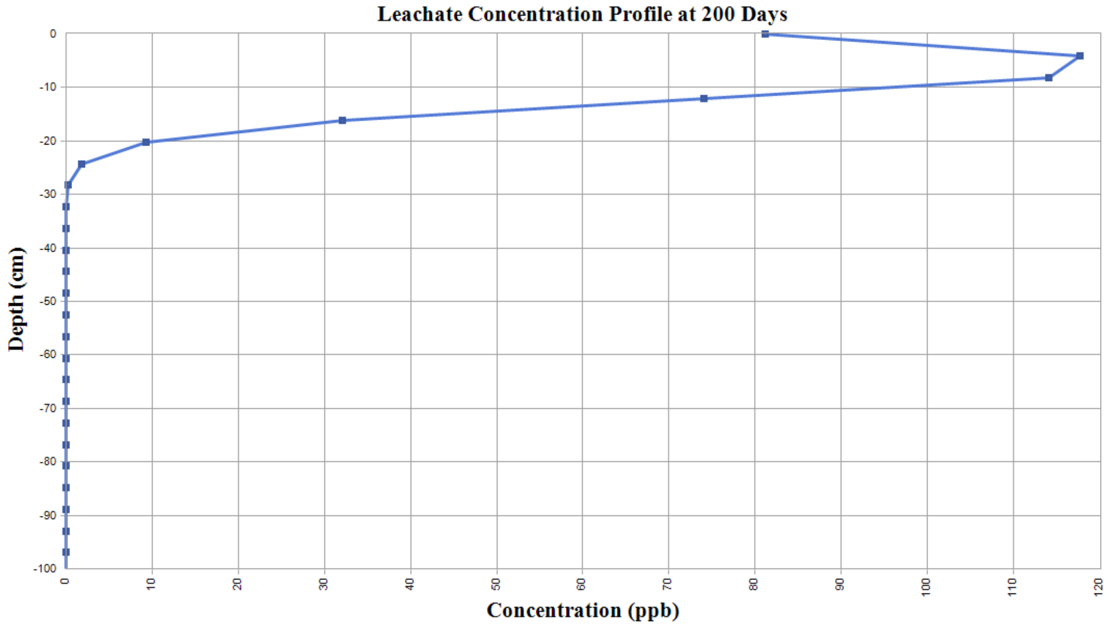


figure 31: Case 2: Leachate Concentration Profile at 200 Days

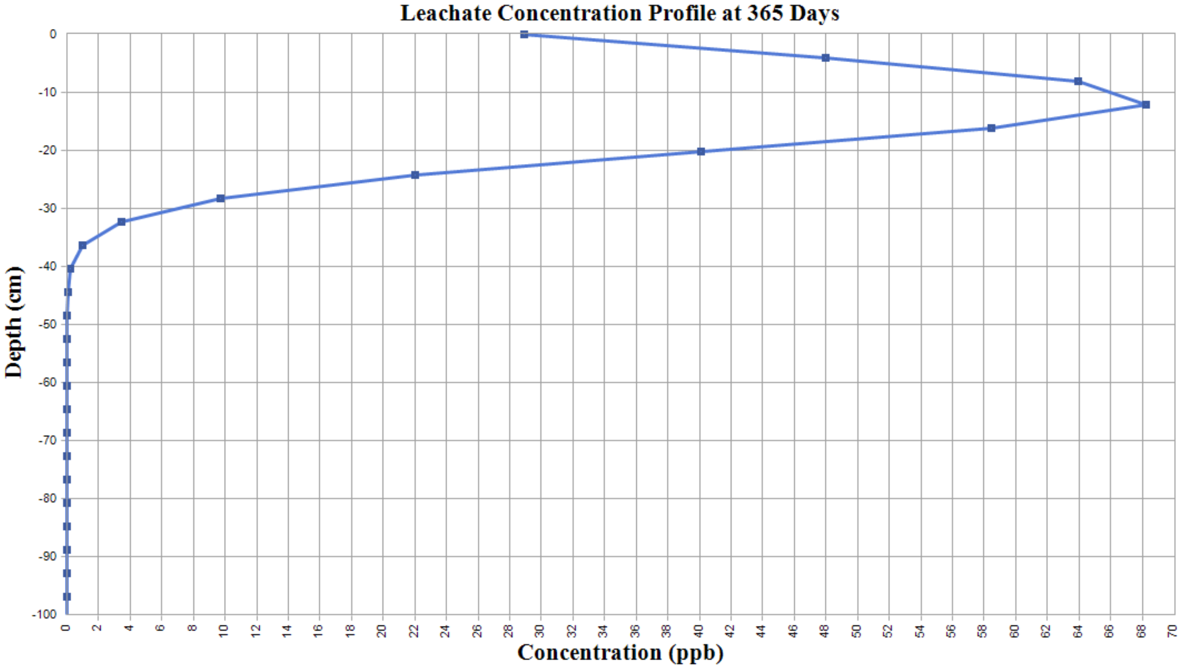


figure 32: Case 2: Leachate Concentration Profile at 365 Days

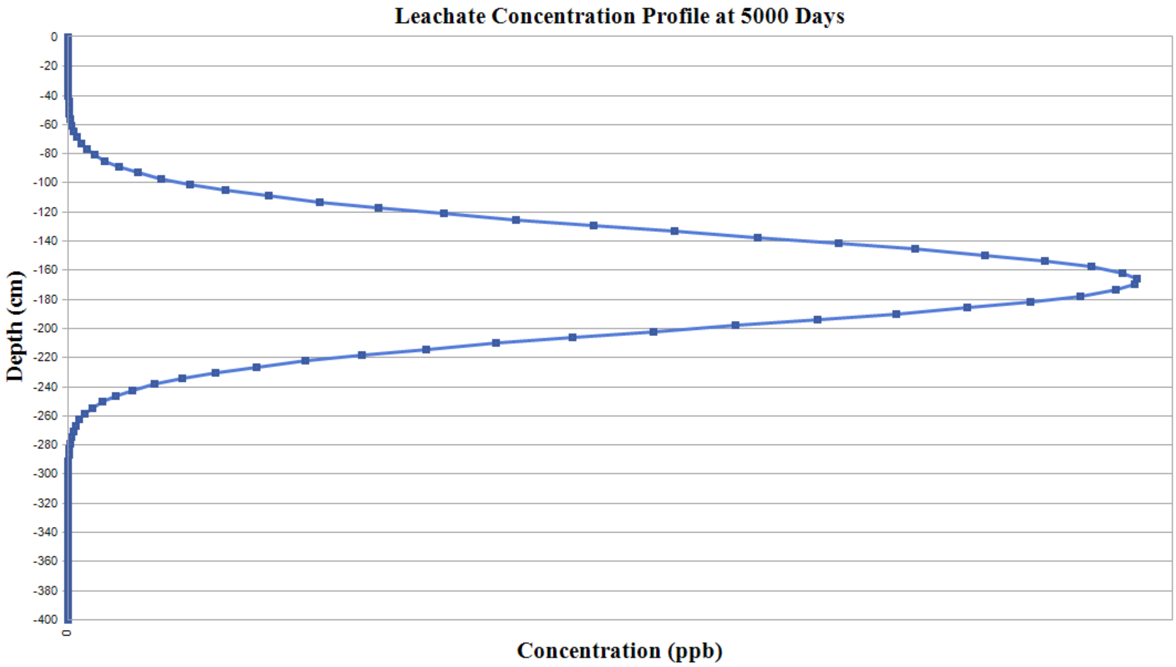


figure 33: Case 2: Leachate Concentration Profile at 5000 Days

e) CASE 3: Sandy Loam; increased waste application rate: 3 [kg/ha]

Water Solubility: 1.4 [mg/L] at 25°C.

Recharge: 450 [mm/yr] = 0.00514 [cm/hr].

Sorption Constant (K_d): f_{om} = 0.0071 for sandy loam, K_{oc}=360 [L/kg] → K_d=2.556

Solid-phase degradation rate constant (k_s): 0.063 [rate/hr]

Liquid-phase degradation rate constant (k_l): 0.001 [rate/hr]

Bulk Density (ρ_b): 1.335 [g/cm^3]

Saturated Water Content (θ_{sat}): mean of 0.435 [cm^3/cm^3] for sandy loam

Characteristic Curve Coefficient (b): 4.90 for sandy loam

Saturated Hydraulic Conductivity (K_{sat}): mean: 4.42 [cm/hr] for sandy loam

Dispersion Coefficient (D): 0.06 [cm^2/day]

Minimum x-value: 0 [cm]

Maximum x-value: 500 [cm] (varies)

Minimum time value: 0 [days]

Maximum time value: 1000 [days] (varies)

Time values: 50 [days]

Number of applications of waste: 1

Waste application rate and starting time: 3 [kg/ha]

Comparing the following figure with the two graphs for the Leachate Concentration Profile at 200 Days from Case 1 and Case 2, increase of application can be seen in the increase of concentration. The maximum concentration at that time increase from about 120 ppb (Case 2 – 1 [kg/ha] applied) to about 240 ppb (Case 1 – 2 [kg/ha] applied) to nearly 360 ppb (Case 3 – 3[kg/ha] applied). The depth of the maximal concentration stays the same with about 5 cm.

Figure 35 in comparison to the analog figures of Case 1 and Case 2 illustrates the leachate flux in total mass. The first impression is that it looks really similar: the development of distribution over the time of Total Mass In, Total Mass Out and Total Mass Remaining is the same as in the other two cases. Differences can be seen in the amount with a maximal Leachate Total Mass of 8.0E-008 in Case 3.

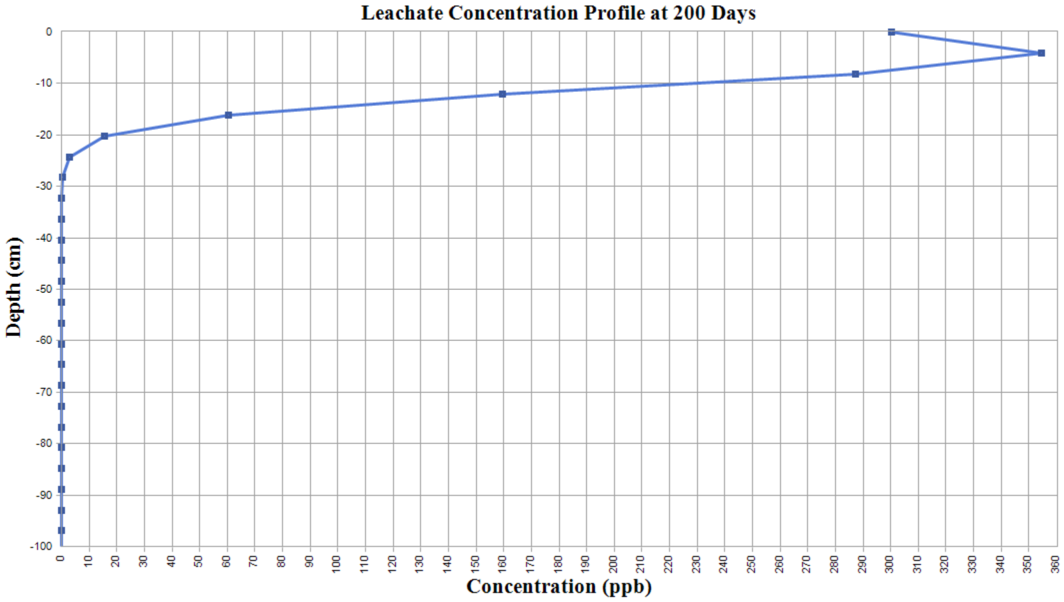


figure 34: Case 3: Leachate Concentration Profile at 200 Days

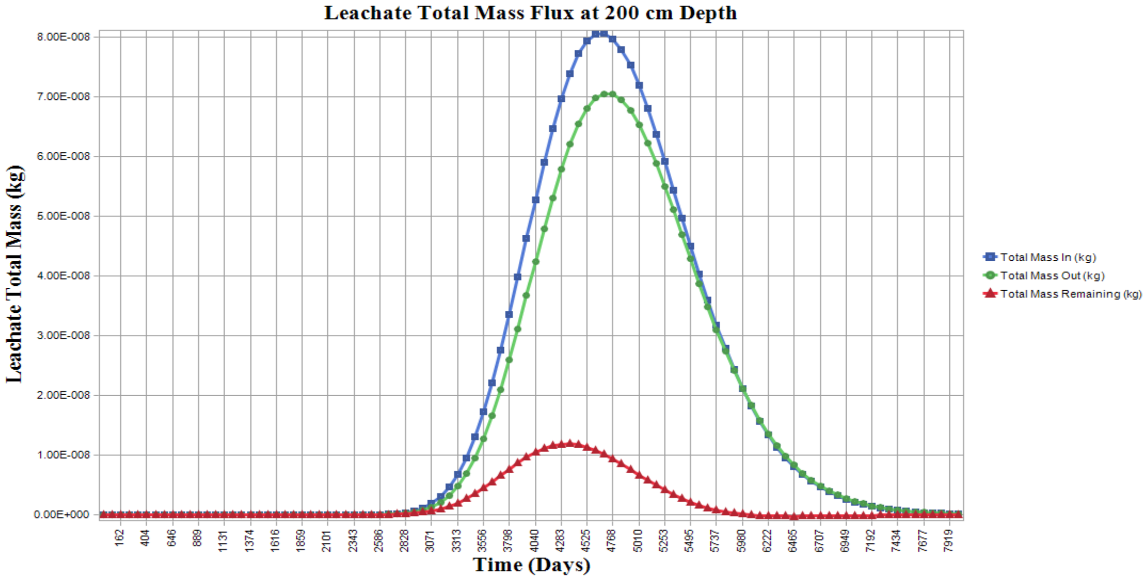


figure 35: Case 3 Leachate Total Mass Flux at 200 cm Depth

f) CASE 4: Loamy sand; waste application rate: 2[kg/ha]

Water Solubility: 1.4 [mg/L] at 25°C.

Recharge: 450 [mm/yr] = 0.00514 [cm/hr].

Sorption Constant (K_d): f_{om} = 0.0061 for loamy sand, divided by 1.724 K_{oc}=360 [L/kg]

Solid-phase degradation rate constant (k_s): 0.063 [rate/hr]

Liquid-phase degradation rate constant (k_l): 0.001 [rate/hr]

Bulk Density (ρ_b): 1.62 [g/cm^3]

Saturated Water Content (θ_{sat}): 0.41 [cm^3/cm^3] for loamy sand

Characteristic Curve Coefficient (b): 4.38 for loamy sand

Saturated Hydraulic Conductivity (K_{sat}): 14.59 [cm/hr] for loamy sand

Dispersion Coefficient (D): 0.06 [cm^2/day]

Minimum x-value: 0 [cm]

Maximum x-value: 500 [cm]

Minimum time value: 0 [days]

Maximum time value: 1000 [days]

Time values: 50 [days]

Number of applications of waste: 1

Waste application rate and starting time: 2 [kg/ha]

As illustrated by the following figure, a change in the soil type (sandy loam – loamy sand) results in a higher concentration of the Leachate Breakthrough Curve. *Figure 36* can for example be compared with *figure 26*; there the maximum of concentration of the Leachate Breakthrough Curve is about 9.50E-003 (Case 1) in case of about 4.00E-002 (Case 3). So a change of the soil type from sandy loam to loamy sand with reference value according to the PESTAN Program means an increase of contaminant concentration of the leachate water.

Observing *figure 26* and *figure 36* also a difference in time at which the maximal concentration occurs can be seen. Whilst in a sandy loam the peak of concentration in

200cm depth is estimated to appear after about eleven years (about 4600 days) in loamy sand this maximum arrives at the same depth after about fourteen years (5150 days).

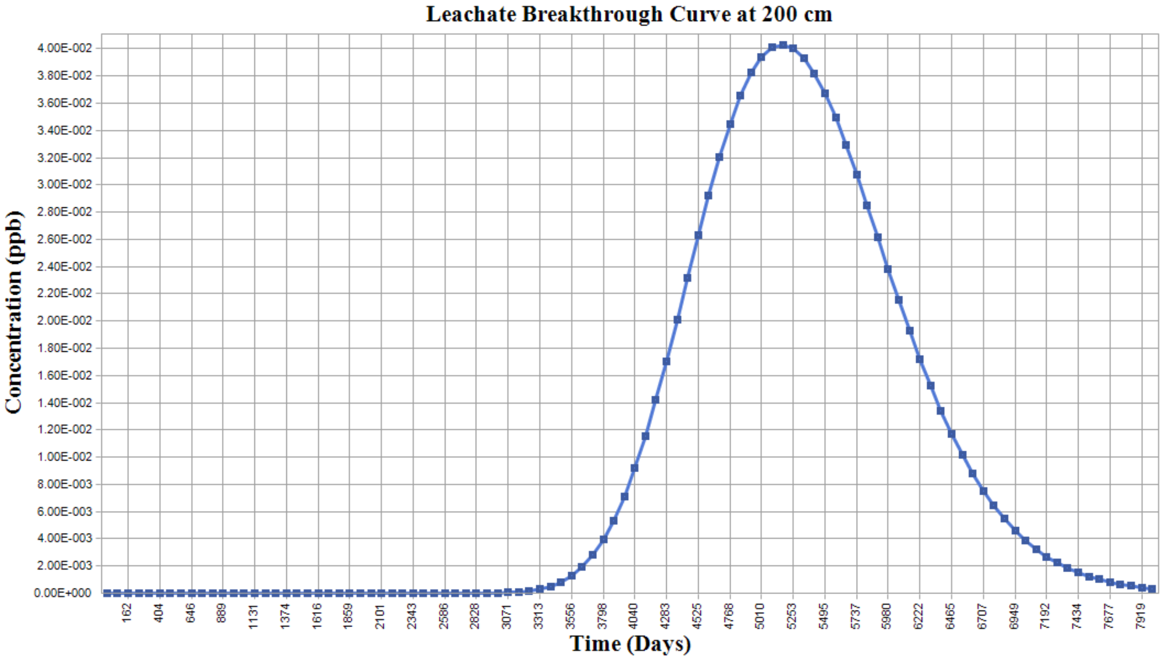


figure 36: Case 4:Leachate Breakthrough Curve at 200 cm

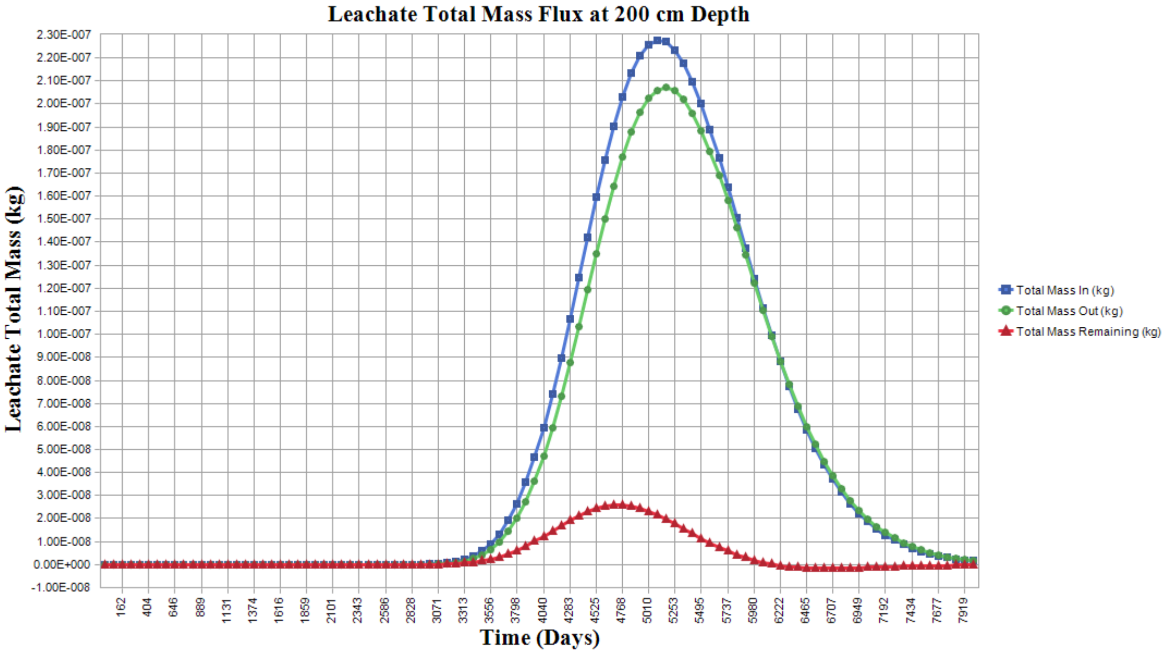


figure 37: Case 4: Leachate Total Mass Flux 200 cm Depth

g) CASE 5: Loamy sand; decreased waste application rate: 1 [kg/ha]

Water Solubility: 1.4 [mg/L] at 25°C.

Recharge: 450 [mm/yr] = 0.00514 [cm/hr].

Sorption Constant (K_d): f_{om} = 0.0061 for loamy sand, divided by 1.724 K_{oc}=360 [L/kg]

Solid-phase degradation rate constant (k_s): 0.063 [rate/hr]

Liquid-phase degradation rate constant (k_l): 0.001 [rate/hr]

Bulk Density (ρ_b): 1.62 [g/cm^3]

Saturated Water Content (θ_{sat}): 0.41 [cm^3/cm^3] for loamy sand

Characteristic Curve Coefficient (b): 4.38 for loamy sand

Saturated Hydraulic Conductivity (K_{sat}): mean: 14.59 [cm/hr] for loamy sand

Dispersion Coefficient (D): 0.06 [cm^2/day]

Minimum x-value: 0 [cm]

Maximum x-value: 500 [cm]

Minimum time value: 0 [days]

Maximum time value: 1000 [days]

Time values: 50 [days]

Number of applications of waste: 1

Waste application rate and starting time: 1 [kg/ha]

Looking at the results of the calculation of values for pollutant and water conditions within the soil (*Tabulation 1*), it can be recognized that of these five values due to a change in the amount of pesticide applied (Case 1-3; Case 4-5) only the length of pollutant slug changes. Actually it varies proportionally with the mass applied. The more pollutant is applied the longer the slug is estimated to be.

Variations in the soil type result in changes of the projected water content, length of pollutant slug, porewater and pollutant velocity. The variation from sandy loam to loamy sand in the soil type results in a decreasing projected water content and a slightly reduced length of pollutant slug.

In the following tabulation these results are summarized:

	Projected water content	Pore water velocity [cm/hr]	Pollutant velocity [cm/hr]	Length of pollutant slug [cm]	Mass decayed prior to recharge [kg]
Case 1	0.257E+00	0.200E-01	0.140E-02	0.389E+01	0.000E+00
Case 2	0.257E+00	0.200E-01	0.140E-02	0.195E+01	0.000E+00
Case 3	0.257E+00	0.200E-01	0.140E-02	0.584E+01	0.000E+00
Case 4	0.209E+00	0.246E-01	0.136E-02	0.379E+01	0.000E+00
Case 5	0.209E+00	0.246E-01	0.136E-02	0.190E+01	0.000E+00
Case 6	0.209E+00	0.246E-01	0.136E-02	0.569E+01	0.000E+00

Tabulation 1: Pollutant and Water conditions within the soil

Interestingly even though pore water velocity is higher in loamy soil, pollutant velocity is smaller. This shows that the fate and velocity of a pollutant also depends on other factors. It could be a result of the lower projected water content in loamy sands when compared to sandy loams. Also the amount of pollutant remaining in liquid phase, as shown in *Tabulation 2,* can be estimated to be higher in sandy loam: due to data of Case 1 in loamy sand 0.104 [kg] which are about 7% of the total pollutant mass remaining (1.48 [kg]). In comparison in sandy loam, in the example of Case 4, 0.0878 [kg] pollutant are remaining in liquid phase, this is about 5.5% of the total pollutant mass that remains (1.59[kg]).

In the following tabulation the results of mass balance after one hundred and fifty days are summed up (Maximum x-value: 500 [cm], Maximum Time value: 8000 [Days]):

	Pollutant remaining in liquid-phase [kg]	Pollutant remaining in solid-phase [kg]	Total mass of pollutant remaining [kg]	Liquid-phase decay of pollutant [kg]
Case 1	0.104	1.38	1.48	0.424
Case 2	0.0526	0.700	0.752	0.215
Case 3	0.151	2.01	2.16	0.618
Case 4	0.0878	1.50	1.59	0.350
Case 5	0.0441	0.752	0.796	0.176
Case 6	0.130	2.21	2.34	0.516

Tabulation 2: Mass balance

Obviously, as also confirmed according to the tabulation value, in total numbers the more pollutant is added to the soil the more is remaining in the different phase and the higher also is the total amount of liquid phase decay of the pollutant. Referring to this data a higher rate of liquid-phase decay in sandy loam than in loamy sand can be estimated. It should be noted that the sum of the total mass of pollutant remaining and the loss of pollutant due to decay must no equal the total pollutant mass applied as several other processes and conditions such as decay prior to infiltration also have to be considered.

Concerning the different types of soil as liquid phase decay of the pollutant is higher in sandy loam, remaining mass of the pollutant is higher in loamy sand.

The different concentration level (C_s, C_w, C_{tot}) do also vary depending on the mass of pesticide applied as well as the soil type. Reviewing the results of the concentration calculations at different times, which can be consulted in *Appendix E*, it can be estimated that the variations in mass are slightly more significant when applied to loamy sand than to sandy loam.

h) CASE 6: Loamy sand; increased waste application rate: 3 [kg/ha]

Water Solubility: 1.4 [mg/L] at 25°C.

Recharge: 450 [mm/yr] = 0.00514 [cm/hr].

Sorption Constant (K_d): f_{om} = 0.0061 for loamy sand, divided by 1.724 K_{oc}=360 [L/kg]

Solid-phase degradation rate constant (k_s): 0.063 [rate/hr]

Liquid-phase degradation rate constant (k_l): 0.001 [rate/hr]

Bulk Density (ρ_b): 1.62 [g/cm^3]

Saturated Water Content (θ_{sat}): 0.41 [cm^3/cm^3] for loamy sand

Characteristic Curve Coefficient (b): 4.38 for loamy sand

Saturated Hydraulic Conductivity (K_{sat}): mean: 14.59 [cm/hr] for loamy sand

Dispersion Coefficient (D): 0.06 [cm^2/day]

Minimum x-value: 0 [cm]

Maximum x-value: 500 [cm]

Minimum time value: 0 [days]

Maximum time value: 1000 [days]

Time values: 50 [days]

Number of applications of waste: 1

Waste application rate and starting time: 3 [kg/ha]

Figure 38 and *figure 39* in comparision to the analog figures of Case 3 (*Appendix E*) also illustrate the different developments of the Leachate Concentration Profile due to different soil types and time levels. After about thirteen and a half year (5000 Days) the peak of concentration is in both soil types at a depth of about 160cm, difference however can be seen in the concentration level. In sandy soil as assumed in Case 3 the concentration maximum at that time is about 2.33E-02 ppb at a depth of around 166 cm. In Case 6 this value is calculated to be 0.146 at a slightly smaller depth of 162 cm.
After only one year this values amount 200.13 ppb at a depth of 8 cm (Case 3) and 248.63 ppb at a depth of 10 cm (Case 6).

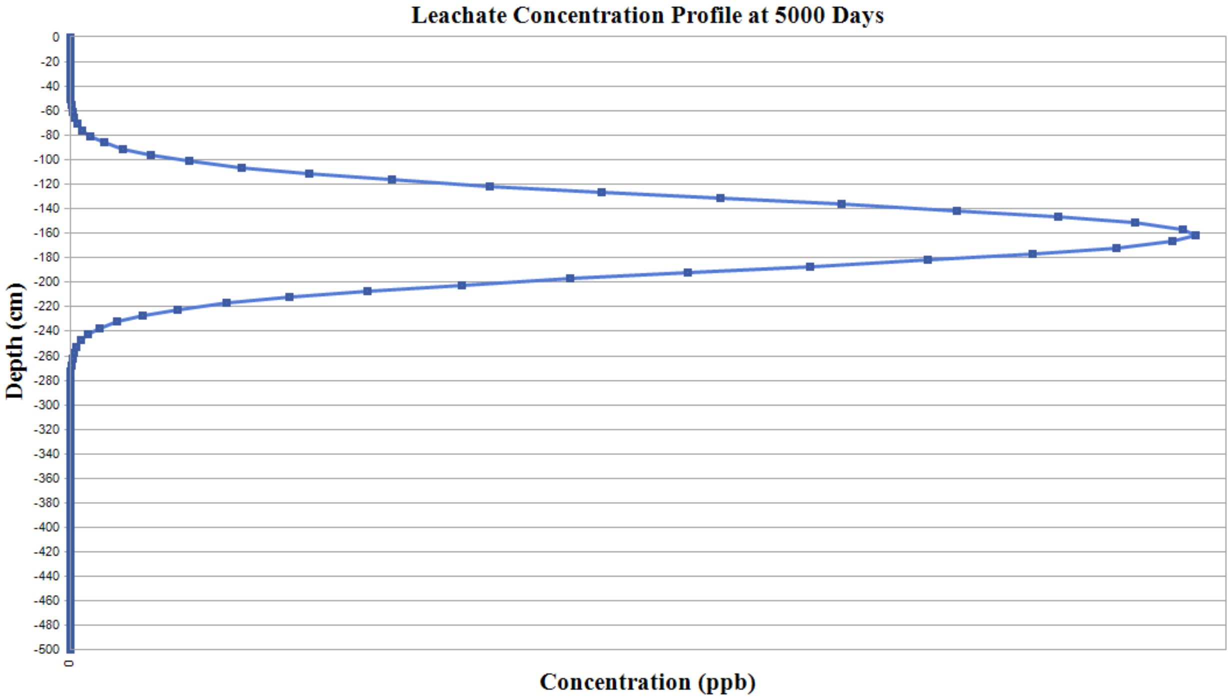


figure 38: Case 6: Leachate Concentration Profile at 5000 Days

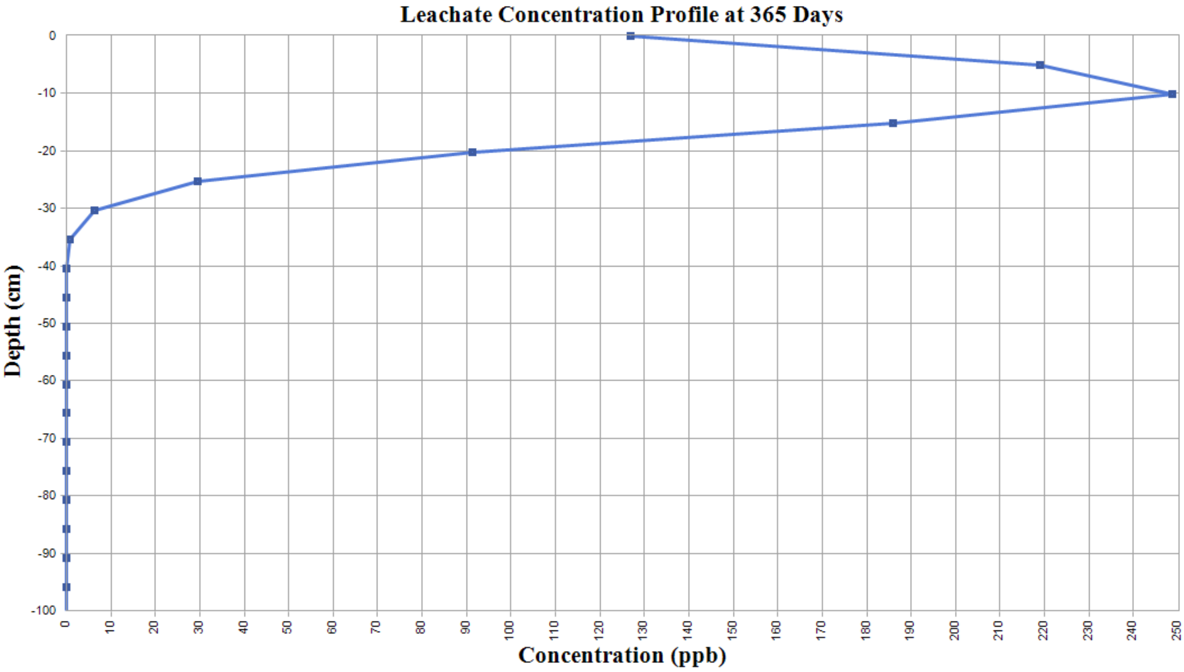


figure 39: Case 6: Leachate Concentration Profile at 365 Days

6. Conclusions

a. Use of pesticides

To be able to satisfy worldwide food demand, as described in *Chapter 2*, in the future an increasing food production will be needed. Pesticides play an important role as they help to control all kinds of insects, herbs, fungus etc. Otherwise huge parts of our crops are likely to be affected by a variety of pests and an irreplaceable loss of food supply is probable.

However pesticides have an alarming and yet not completely understood impact on the environment and human health. Soil quality can be deteriorated by an exceeded pesticide application and probably results in an opposed effect so that productivity and field fertility declines. Therefore it is decisive to use them with caution and only in the amounts truly necessary. Testing of pesticide and registration prior to its permission and adoption are fundamental to be able to guarantee a responsible use, for human health and food security now and for future generations.

As a grand variety of different chemicals for pesticide control exists, decisions about the applied pesticide should be taken advisedly. For each type of soil, each crop and different hydrological circumstances another pesticide is the most effective one. Available pesticides should be optimized and tested under numerous conditions to find the ideal mode of application. Also organic farming should be taken into account, where despite the widely spread opinion, also different types of pest controls are used. (Whitmore, Künast and Graff, 2015, p.29) The substances applied however, are less toxic and their impact on as well as their persistence in soils is generally estimated to be less harmful.

b. Models

i. Generally

There is already a huge variety of models available for the estimation and modeling of transport and fate of pesticides in the environment. However, all of them are based on assumption and simplification, which results in inaccurate results and miscalculations. The more precise and reliable the output of the model is the higher is the effort needed to receive adequate input data. At best, in field studies should be made, however, as often resources for expensive and laborious detailed investigations is missing, reference data is consulted.

Enhancement and amplification of this information could be helpful to improve and facilitate the work with contaminant modeling programs.

ii. Pestan

At the example of PESTAN the assumptions taken to be able to apply this program on real data is explained in detail above. Considering the influence small changes in the input have on the results of the model some of them can have significant effect on the output data. As a consequence of that it is important to check the resulting data on reasonableness and possible doubts and errors should be outlined in the conclusion.

The explanations of the required input data for the application in PESTAN are clear and easy to understand, however some values are very detailed and – if not provided by another source - not very easy to find out without having to make field observations. In other cases, as describe in the PESTAN guide, some demanded information can be calculated with different other values, that are probably available more easily. In case that a value cannot be detected or effort to do so is disproportionate, reference values for many input numbers are provided by the program. Strangely, some reference values according to the PESTAN guide (*Appendix B*) do not correspond with the ones presented by the program itself.

Once all the input data is determined, modeling and handling of the program is relatively simple. Variation in the input data, especially time and depth, to receive different figure and graphs is easy. However some options that are probably provided by more modern programs (Min/Max-values, modifications of the x-axe) are not available. Also during the application various warnings and errors appeared rather randomly, but in the end did not really affect the results. When input information was changed, in some cases the output did not adapt immediately, so results must always be checked on reasonableness coherency.

The final output data and further conclusions must be interpreted with caution, always considering the assumptions made prior to the calculations as well as the simplifications of the model calculations itself. If PESTAN model is applied the results can give an idea of how the pesticide will be transported and transformed in the environment. Nonetheless to get a reliable conclusion and to take measure concerning pesticide control additionally consideration of other models should be taken and comparison of the results may be made.

c. Results of the application: Chlorpyrifos in Aldaia

As an example for the application the plain of Valencia, more precisely Aldaia, was chosen. In this region various crops of different types of citrus fruits as well as vegetables are common. Chlorpyrifos is a widely used pesticide for this type of crops.

The data is based on real data but as efforts to achieve exact information for some parameters where high, some assumptions where made and reference data from the program was consulted. Therefore the results should be seen as a possible scenario of the transport and fate of this pesticide, to be able to analyze and check the functionality of the PESTAN program and its results.

Due to the data the conclusion could be made as follows, also depending of the information needed: PESTAN simulates that Chlorpyrifos moves relatively slowly in both types of soil. If for example the time until it reaches the water table is wanted, Leachate Concentration Curve or Leachate Total Mass Flux at the depth of the water table (in this case 5500 cm) can be purchased. In case that the concentration level due to a certain regulation is needed, better the Leachate Concentration Profile is used. With this figure for example it also can be evaluated if the prescribed time lapse between discharge of the contaminant and harvest of the crop is reasonable.

Basic information about the pesticide Chlorpyrifos can be illustrated easily with this model, and can serve as an overview of the pesticides impact. As a basis for further measures input data must be investigated more precisely and related researches should be considered.

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Description of TFG objectives

Groundwater and soil contamination are one of the most relevant environmental issues related with agricultural activities. Organic pesticides are widely used to prevent plagues and assure a desirable quality of the final product. However, the type of pesticide as well as the amount used (dose and concentration) must be justified from the environmental point of view in relation with the type of crops, soil characteristics and vulnerability of the underground exposed aquifer.

The main objective of the study is to obtain practical knowledge about the state-of-the-art of the mathematical models used to simulate contamination processes caused by organic pesticides.

The use of these models will provide valuable information to the decision-makers in order to define the practical conditions under which organic pesticides could be used to ensure the environmental regulations.

Appendix A – UN Resolution 64/292: Human right to water and sanitation

Appendix B – Pestan Guide

Appendix C – Approximating Pollutant Transport to Groundwater

Appendix D – Chlorpyrifos – Technical Fact Sheet (NPIC)

Appendix E – Results of the application: Chlorpyrifos in Aldaia, Valencia