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Master's thesis

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Sorption and leaching of artemisinin in soils using the DAISY-model

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Declaration of authorship

I hereby declare, that this master thesis with the title »Sorption and leaching of artemisinin in soils using the DAISY-model« has been composed by myself, and describes my own work unless stated otherwise in the text. All sentences, passages as well as all sources of information derived from other people’s work have been specifically cited.

Place, Date	Signature

Preface and acknowledgement

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…and very important, my family and friends at home: zaga hoo David! Made it much easier with you!

Daniel Hillel in ‘Environmental Soil Physics’ about the unsaturated water flow in soils and another important issue concerning this work and its content:

“The ideal state of equilibrium, like human happiness, may never be achieved in practice, but its natural pursuit is a universal rule.”

Abstract

Artemisinin, a bioactive compound produced and released by the plant *Artemisia annua*, is used worldwide for medical malaria treatment. The plant is increasingly cultivated globally in order to meet the worldwide demand. Research exhibited that artemisinin can have toxic effects in the aquatic and terrestrial environment and thus need to be planted and used with caution. Up to now, no scientific exploration was carried out to investigate the fate and behaviour of artemisinin in soils. In a field study, artemisinin was found in two-meter deep drainage pipes, which sparked further interest. Consequently, this master thesis observes experimentally the sorption properties and mechanism of artemisinin in soils. Additionally, simulations were carried out using the DAISY model to determine if artemisinin is able to leach to the groundwater and if it is capable to exceed the EC10 and EC50 for *Lemna minor* and *Pseudokirchneriella sp*. Finally, sensitivity analyses were performed to estimate potential important factors when considering artemisinin leaching in soils.

Sorption batch experiments were carried out with sandy and sandy loam top- and subsoil from study fields in Taastrup (DK) and Jyndevad (DK). The sorption data, together with reliable and site-specific values and expert opinions were used to parameterize DAISY. As a final point, sensitivity analyses were carried out in order to allocate important factors influencing leaching simulation of artemisinin.

The results showed weak sorption capacity of artemisinin in both soils and revealed partitioning into SOM as the main sorption mechanism. For the sandy soil, the Ap-horizon possessed a K_F-value of 0.58 L kg^{-1} and the C-horizon 0.3 L kg^{-1}. The sandy loam soil Ap-horizon had a K_F of 0.61 L kg^{-1} and the Bt-horizon 0.31 Lkg^{-1}. As the SOM declines, surface complexation on clay particles takes place. However, the results of the sorption batch equilibrium method revealed uncertainties which can be further improved by raising the matrix/solution ratio and setting up a better matrix extraction method.

There was no leaching of artemisinin to the upper groundwater observed in the sandy soil with the DAISY simulation. As well, the sandy loam soil revealed no exceedance of the ecotoxicological threshold but, due to preferential flow, a substantial amount of artemisinin was bypassing, the degrading upper soil matrix after an intensive rain event. Thus, macropores, drainage pipes, the load and climatic conditions are considered to be important. It is inevitably necessary to conduct further site-specific risk assessments, adapted to climatic, genetic, managerial and local soil conditions, before any final conclusion upon the effects of artemisinin leaching to the groundwater can be drawn. Furthermore, potentially important factors such as runoff, subsurface degradation, photolysis, and colloids were omitted and need to be incorporated when necessary. Finally, it is recommended to conduct field experiments to verify the modelled outcome in order to create reliable risk assessments.

Zusammenfassung

Artemisinin, ein bioaktiver sekundärer Pflanzenstoff produziert von *Artemisia annua,* wird weltweit für die medizinische Behandlung von Malaria eingesetzt. Durch die steigende Nachfrage wird die Pflanze zunehmend global angebaut. Forschungen zeigen jedoch, dass Artemisinin toxische Auswirkungen auf gewisse aquatische und terrestrische Lebewesen ausüben kann und es muss daher mit Vorsicht produziert werden. In einer Feldstudie wurde Artemisinin in 2 Meter tiefen Drainagen Röhren gefunden und ausserdem sind bis heute noch keine wissenschaftliche Forschungen durchgeführt worden, die den Verbleib und das Verhalten von Artemisinin in Böden untersucht. Deswegen untersucht diese Masterarbeit experimentell die Sorptions-Eigenschaften und Mechanismen von Artemisinin in Böden. Weiter wurde mit dem Umwelt-Modell DAISY Auswaschung-Simulationen durchgeführt und beobachtet, ob Artemisinin den EC10 und EC50 für *Lemna minor* und *Pseudokirchneriella sp.* überschreitet. Schlussendlich sind Sensitivitätsanalysen durchgeführt worden um wichtige Faktoren die zu erhöhten Konzentration im Grundwasser führen könnten erkennen zu können.

Die Sorption Experimente wurden mit einem sandigen, und einem sandig-lehmigen Ober- und Unterboden aus Taastrup (DK) und Jyndevad (DK) durchgeführt. Weiter wurden die Sorption-Daten zusammen mit zuverlässigen und ortsspezifischen Werten verwendet, um DAISY zu parametrisieren, und danach Sensitivitäts-Analysen durchzuführen.

Die Ergebnisse zeigten ein schwaches Sorptionsvermögen von Artemisinin in beiden Böden und offenbarte Partitionierung in die organische Bodensubstanz als den hauptsächlichen Sorptionsmechanismus. Der Ap-Horizont vom sandigen Boden besaß einen K_F-Wert von 0,58 L kg $^{-1}$ und der C-Horizont einen Wert von 0,3 L kg^{-1}. Der Ap-Horizont vom sandig lehmige Boden hatte einen K_F-Wert von 0,61 L kg^{-1} und der Bt – Horizont einen Wert von 0,31 L kg^{-1}. Weiter wird vermutet wenn der organische Gehalt im Boden sinkt, nimmt die Oberflächen-Komplexierung auf Tonpartikeln zu. Allerdings zeigten die Ergebnisse der Sorption Experimente Unsicherheiten, die mit der Anhebung des Matrix / Lösungs-Verhältnisses und einem neuen Matrix-Extraktions-Verfahren verbessert werden könnten.

Es wurde keine Auswaschung von Artemisinin zum oberen Grundwasser im sandigen Boden beobachtet. Auch im sandig lehmigen Boden gab es keine Überschreitung des ökotoxikologischen Schwellenwertes, aber aufgrund von Makroporen konnte eine erhebliche Menge von Artemisinin, nach einem starken Regen-Ereignis, die bioaktive obere Bodenmatrix überwinden und so im Unterboden oberhalb dem Grundwasser sich akkumulieren. Deswegen sind Makroporen, Drainage-Rohre, aber auch die Freisetzungsrate (Ladung) und klimatischen Bedingungen sind wichtige Faktoren, die die Auswaschung zum Grundwasser beeinflussen.

Es ist unvermeidlich weitere ortsspezifische Risikoeinschätzungen durchzuführen, angepasst an die klimatischen, genetischen, betrieblichen und lokalen Boden-Verhältnisse bevor endgültige Schlussfolgerungen über die Produktion von Artemisinin gezogen werden können. Ausserdem wurden bei der Simulation wichtige Faktoren wie der Oberflächen-Abfluss, die Mineralisierung im Unterboden, die Photolyse auf der Bodenoberlfäche, und Kolloid-Transport ausgelassen. Wenn nötig müssen diese Faktoren bei zukünftigen Simulationen miteinbezogen werden und es empfiehlt es sich für die Validierung der Resultate Feldversuche durchzuführen.

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1. Introduction

1.1 Background and objectives

Leaching of pesticides in agriculture soils may be of high relevance due to their toxicity to humankind and the environment. In the past, several kinds of artificially-produced chemical products have been found in surface- and groundwater bodies all over the world, even though these sites are often considered to be the most important sources of drinking water (Hancock et al., 2008 and Whiteacre, 2013). For example, in Europe the pesticide loads frequently exceeded the drinking water limit set by the EU at 0.1 µg L^{-1}, which led to rigorous testing of each pesticide before entering the markets (EU, 1991). The investigation procedure usually contains a combination of sophisticated computer simulations and data from field experiments (Vanclooster et al, 2000). Modelling is well suited to evaluate the risk of pesticides leaching to the groundwater (Whiteacre, 2013), because it is an economic way of assessing the behaviour of pesticides under field conditions and it is cheaper and faster than laborious and time-consuming field experiments (Boesten, 1999).

Despite all those efforts to create cleaner and more modern agriculture practices, not much research has been carried out regarding natural toxins and their fate and behaviour in the environment. Natural toxins are usually produced in plants as secondary metabolites, not directly determined for the metabolism and therefore having specific ecological function, such as helping plants cope with threats like herbivory or microbial attacks (i.e., allelopathy). Consequently, they present toxic effects to their surrounding environment. Examples are the norsesquiterpene glycoside ptaquiloside (PTA) from the invasive bracken fern (genus *Pteridium*) and the well-known monoterpene thujone produced by the western red cedar (*Thuja plicata* L.) (Shahin et al., 1999 and Strobel et al., 2005). Both PTA with its low sorption capacity and thujone with its high resistance against degradation might also be prone to leaching under certain circumstances (i.e., heavy rain storm) and therefore pose a substantial risk in surface and groundwater contamination when occurring on a large scale (Rasmussen et al., 2002 and Strobel et al., 2005). Even though cultivated and naturally occurring on agriculture fields, forests and other natural sites, extensive environmental risk assessments such as for the above-mentioned pesticides, are lacking. Monocultures releasing excessive amounts of natural toxin are used for increased food and biomedical production. According to Hermann et al. (2012) and Vines (2006), around 80% of the world's population depend on herbal medicine as primary health care, which leads to large-scale cultivation and subsequently to an enhanced concentration of corresponding active metabolites in the environment.

One such example of an increasing cultivation of an herbal medicine plant is *Artemisia annua* L., also known as sweet wormwood or qinghao, which has been used for more than 2000 years in China for treating many diseases including malaria (WHO, 2006). The reason for its antimalarial effect is artemisinin, a secondary metabolite containing an active endoperoxide bridge which is the reason for its healing character (Meschnick et al., 1996). Since the 1970s, the plant has been increasingly cultivated due to its efficiency, but also because even today no method exists to artificially synthesise artemisinin in an economically reasonable way (WHO, 2006 and Arsenault et al., 2008).

However, according to several studies, artemisinin exhibits toxic impact on the terrestrial and aquatic environment when exceeding certain concentration thresholds (Jessing et al. 2009a, Duke et al., 1987, Morvillo et al., 2011 and Hermann et al., 2012). Moreover, it possesses similar chemical properties to pesticides, such as atrazin, terbulthylazine, or metholachlor (e.g., lipophilicity, half-lives, water solubility), and should therefore be treated as one (Jessing et al., 2009a). The combination of chemical properties and toxicity determines the leaching potential of artemisinin and its threat to ground and surface waters (Jessing et al. (2009a). During their field work and after a heavy rain shower, Hermann et al. (2012) detected artemisnin in 200 cm deep drainage pipes (oral note). This incident and the fact that so far no research has been conducted investigating the leaching behaviour of artemisnin in soils, was the starting point of the present thesis.

The aim of this Master thesis is to get a better overall and principle understanding of the fate and behaviour of artemisnin in soils and conduct a simple risk assessment. The work is structured into two parts. Firstly, sorption studies of artemisinin on a sandy (Jynedvad, DK) and sandy loam soil (Taastrup, DK) were carried out to gain a better insight in the sorption behaviour of artemisinin and to develop a database for the modelling process. Secondly, simulations with the DAISY model were performed with parameters of two experimental soils, the experimental determined sorption properties, recently conducted laboratory and field experiments, and experts' experiences. The parameterisation of the model was chosen to be rather simple but with the most important, reliable and robust parameters. Finally, two simple 'one-at-a-time-sensitivity analyses' were conducted with a lowered half-life (DT50) in the sandy loam soil (scenario 1), and an increased artemisinin load for both soils (scenario 2). The intention was to guide future research efforts, and to explore how changed input parameters affect the output and, in this way, if one is insignificant or unimportant and can be eliminated (Hamby, 1994).

Specific research questions are: i) what kind of sorption properties and mechanisms does artemisinin exhibit in the sandy and sandy loam soils, ii) and is artemisinin able to leach to the groundwater in both sandy and sandy loam soil and, if yes, is it capable of exceeding the EC10 and EC50 for *Lemna minor* and *Pseudokirchneriella sp.*? iii) Finally, what are potentially important factors when considering artemisinin leaching in soils?

1.2 Natural toxin artemisinin

1.2.1 Malaria- a deadly disease

Malaria, a mosquito-borne infectious disease to humans, kills a child every minute and infects around 219 million people every year (UNICEF, 2013 and Olliaro and Taylor, 2004). Despites its massive negative impact on economic development, it is also the disease of poverty and appears mostly in rural regions where people are living in poorly constructed dwellings that only offer few, if any, barriers against mosquitoes (UNICEF, 2013). It occurs mainly in tropical regions such as Africa, India, Indonesia, and the Amazon region of Latin America. The parasites of the genus Plasmodium, transferred through a bite of the four different mosquito species: P.flaciparum, P. vivax, P. ovale and P. malariae is responsible for the malaria disease (WHO, 2012 and Heemskerk et al., 2006). The aforementioned parasites rapidly multiply in the human liver from where they are transferred to red blood cells. Subsequently, the parasites weaken the immune system and cause serious complications that could lead to death.

According to World Health Organization (2012), artemisinin-based combination therapy (ACT) is the most promising anti- malaria drug currently available to curtail the malaria disease. The ACT treatment is a combination of anti-malaria drugs, including artemisinin and its derivatives artesunate, arthemether and a metabolite dyhydroartemisinin that are able to rapidly kill most of the Plasmodium parasites (Olliaro and Taylor, 2004 and Heemskerk et al., 2006).They are all belonging to the endoperoxides, a promising class of antimalarial drugs which may meet the dual challenges posed by drug- resistance parasites and the rapid progression of malarial illness (Meschnick et al., 1996). Furthermore, they have numerous advantages over existing antimalarial drugs such as no cross-resistance with other antimalarial drugs and the clearance of the infected blood is more rapidly (Meschnick et al., 1996).

Artemisinin is a rare sesquiterpene lactone with an endoperoxide bridge (C-O-O-C) which is unique among the antimalarial drugs (Meschnick et al., 1996). According to the same authors (Meschnick et al., 1996), only the endoperoxide bridge is responsible for the antimalarial activity whereas the complex ring structure is not (see figure 1).

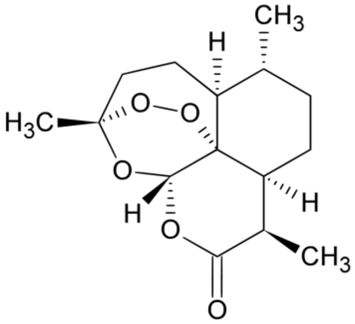

Figure 1: Chemical structure of artemisinin according to Lui et al. (1979).

Once crossed specific parasite's membrane, the mechanism of artemisinin includes activation and alkylation (Jessing et al. 2009a). According to Meschnick et al. (1996), the activation is made by reductive cleavage of the peroxide bond, facilitated by Fe(II), leading to the formation of oxygen- centred radicals. The alkylation is compromised by the formation of adducts between the released free radical and electrophilic intermediate with malaria target proteins (Meschnick et al., 1996).

Much hope has been put into the healing character of *A.annua* and its secondary metabolites also because the drug group around artemisinin is considered to be the most important since World War II (Meschnick et al., 1996). Effective anti-malaria drugs are costly and the ones which are affordable to the people have become ineffective because the parasites have developed resistance to them (Heemskerk et al., 2006). A lot of endeavour was shown in order to make the use of ACT more widespread and by increasing the cultivation of A.annua, especially in the parts of the world where it is mostly needed (e.g. rural areas). According to Heemskerk et al. (2006), it is technically possible to cultivate sufficient amount of *A.annua* to produce enough ACTs and to cure all the malaria patients in the world.

1.2.2 Production and release of artemisinin by *Artemisia annua* L.

With the exception of *Artemisia apiacae, A. annua* appears to be the only plant that produces artemisinin (Verma et al., 2011). A. annua originates from China but became naturalized in many countries all over the world and is cultivated today especially in China, Vietnam, India, Kenya, Tanzania and Eastern Europe (Heemskerk et al., 2006 and Ferreira et al., 1997). It is a shrub, reaching more than 2 m in height (Ferreira et al., 1997) and generates on average between 0.01% and 0.4% artemisinin of plant dry weight (Janick and Ferreira, 1996). According to Meshnick et al. (1996), new varieties are able to produce up to 2 % artemisinin (dry weight). Converted into kg ha^{-1}, artemisinin yields vary from 1.5 to 10 kg ha^{-1} in Europe and Africa, but can reach up to 90 kg ha-1 in Asia by multi-harvesting (Kumara et al., 2004). The production depends on various environmental factors such as genetics (Ferreira et al., 2005), UV-B and UV-C radiation (Rai et al., 2011), moderate drought (Marcese et al., 2010), agricultural management (Kumara et al., 2004) and others such as nutrient deficiency (Jessing, 2012b).

The majority of artemisinin is stored in glandular trichomes on the leaves which burst when mature, or by external forces such as rain drops (see figure 2) (Duke and Paul, 1993). But it has also been detected in leaves, small green stems, buds, flowers, and seeds (Ferreira, 1997), and to a minor extent, in roots (Jessing et al., 2012).

According to Ferreira et al. (1997), the production peak of artemisinin in A.annua is found during flowering. According to Jessing et al. (2012a) the major, quantitative contribution of the loss of artemisinin to the soil origins from the dead leaves. But it is also released to a minor extent by rain runoff and roots. Furthermore, the soil environment is exposed to continuous artemisinin release and not to single doses as it is with pesticides (Jessing et al., 2013). However, according to Hermann et al. (2012), the distribution of artemisinin in the soil is diffuse and it was detected up to 15 m from cultivated A.annua plants, indicating that wind is a key factor determining the horizontal distribution.

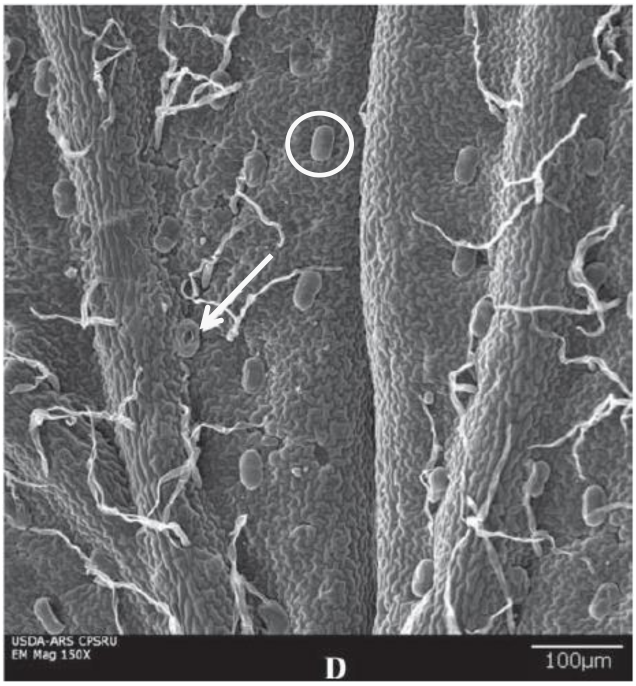

Figure 2: SEM pictures according to Jessing et al. (2012) of the adaxial side of a young *Artemisia annua* leave, with trichomes (white circle) and after a simulated rain event. The white arrow indicates a broken trichome

1.2.3 Toxicity and behaviour of artemisinin in the soil environment

Artemisinin is a secondary metabolite with allelochemical behaviour and can be considered to be a potential risk to non-target organisms in the terrestrial and aquatic environment. Various ecotoxicological analyses have shown its toxicity towards sensitive species living in the surrounding environment. For example, Jessing et al. (2009a) revealed that it inhibits growth of lettuce (*Lactuva sativa*) at relatively low concentrations (EC50, 2.5 mg kg^{-1}). The EC50 for freshwater species such as algae (*Pseudokirchneriella sp.*) and duckweed (*Lemna minor*) revealed values of 0.24 mg L^{-1} and 0.19 mg L^{-1}, respectively. Furthermore, earthworms (*Eisenia fetida*) within the range measured at field studies were repelled (Jessing et al., 2009a). Morvillo et al. (2011) discovered that the soybean production was affected by the presence of *A.annua* in an intercropping system and Hermann et al. (2012) discovered an impact on bacterial activity in soil at relatively low artemisinin concentration. Jessing et al. (2009a) calculated in their study the hazard quotient of artemisinin (PEC/PNEC, including safety factor 1000) and concluded a high environmental risk in cultivating *A. annua* based on their field settings.

Jessing et al. (2009a) pointed out the accumulative character of artemisinin although it possess rather short half- lives in the examined sandy (4.22 days) and loamy soil (0.9 days). Effectively, Jessing et al. (2012) found increasing artemisinin concentration years after a field study. The accumulation might be due to the estimated log K_{OC} of 2.51 and a log K_{OW} of about 2.9 (see table 1) which indicate that artemisinin is sorbing rather strongly into soil organic matter and therefore hindering the degradation (Jessing et al., 2009a). Hermann et al. (2012) measured experimentally a Kd- value of 6.57 L kg^{-1} for a sandy loam topsoil and a K_d of 0.92 L kg^{-1} for the subsoil with a lower SOM- content, which confirms the hydrophobic properties. Due to the hydrophobic character diffusion of artemisnin is expected to be very limited in soils and as well volatilization can be excluded because of the low vapour pressure (see table 1) (Jessing et al., 2013).

However, Jessing et al. (2009b) estimated larger half-lives on the same sandy soil (13.5 days) as above mentioned and on a clay soil (8.3 days). Due to this considerable difference in soil persistency, the mentioned relatively low K_d-values and the medium water solubility will categorize artemisnin as having a leaching potential (Jessing et al., 2009a).

Table 1: Selected chemical properties of artemisinin.

Scientific information:	**Value**
CAS no.	63968-64-9
IUPAC name	(3*R*,5a*S*,6*R*,8a*S*,9*R*,12*S*,12a*R*)-octahydro-3,6,9-trimethyl-3,12-epoxy-12*H*-pyrano[4,3-j]-1,2-benzodioxepin-10(3*H*)-one
Molecular formula	$C_{15}H_{22}O_5$
Molar mass	282.34 g mol^{-1}
Solubility in water	49.7 mg L^{-1} [a]
Henry's law constant K_H	$4.92 * 10^{-9}$ atm * m^3 mol^{-1} [b]
Log K_{ow}	2.90 [b]
Log K_{oc}	2.51 [b]

[a] according to Jessing et al., 2009a,
[b] calculated with EPIWEB v4.0 (US EPA)

1.3 DAISY model description

The purpose of a model is to describe adequately the reality, explain theories and predict the realities as well as possible. The DAISY- model is a soil-plant-atmosphere model focusing on agro- ecosystems (Hansen et al., 2012a). Its origin is from the late 1980's where less expensive agro- ecosystem models were needed than the laborious field and laboratory measurements to predict nitrogen leaching. Since then it was used extensively and was validated in a number major comparative studies (see Abrahamsen, 2011) (Hansen, 2002). It is capable to simulate water, heat, and carbon processes, the nitrogen balance and plant growth, and the fate of agro-chemicals (e.g. solute transport such as pesticides and natural toxins). Furthermore, it is categorized as an explanatory, mechanistic, or physically based model (Hansen et al., 2012a). Even though DAISY is able to simulate two dimensions (2-D) which includes drain flow dynamics, the usage of the less resource requiring one dimensional version (1-D) is sufficient in the current study. Normally, the 1-D model disregards the horizontal flow occurring generally in the vadose zone (Mollerup et al., unpublished). However, in the current study the model is based on a 1-D vertical discretization where the horizontal flow is included as a sink term, and the drain flow based on Hooghoudt theory, is still involved (Abrahamsen, unpublished). Hence the 1-D model is assumed to be sufficiently precise in showing the concentration trend for a chemical element or compound with low sorption capacity within the soil column and drainage flow.

It is the first time that the fate and behaviour of a natural toxin in an agro-ecosystem has been simulated with DAISY. Thus, artemisinin is perceived as a pesticide and the parameterisation process is treated the same way. Several studies have been successfully carried out with DAISY predicting pesticide behaviour in the soil and compared with real field data in order to validate and confirm the applicability and accuracy (Hansen et al., 2010a, Hansen et al., 2010b and Hansen et al. 2012b). Despite its similarities, the most important difference when simulating a natural toxin is its continuous or fluctuating release (e.g. load) over the growing season.

Below the three most important simulation processes applied in the present study are stated.

1.3.1 Hydrological processes

The atmosphere and the groundwater shape the outer boundaries of the soil-water system (Hansen, 2002). Figure 3 presents a schematic overview of the important water processes, driven by the weather and management data. Importance was attached in the present work on precipitation, evapotranspiration, percolation processes from the surface to the soil matrix (including preferential flow), capillary rise, artificial drain flow and storage in the soil matrix.

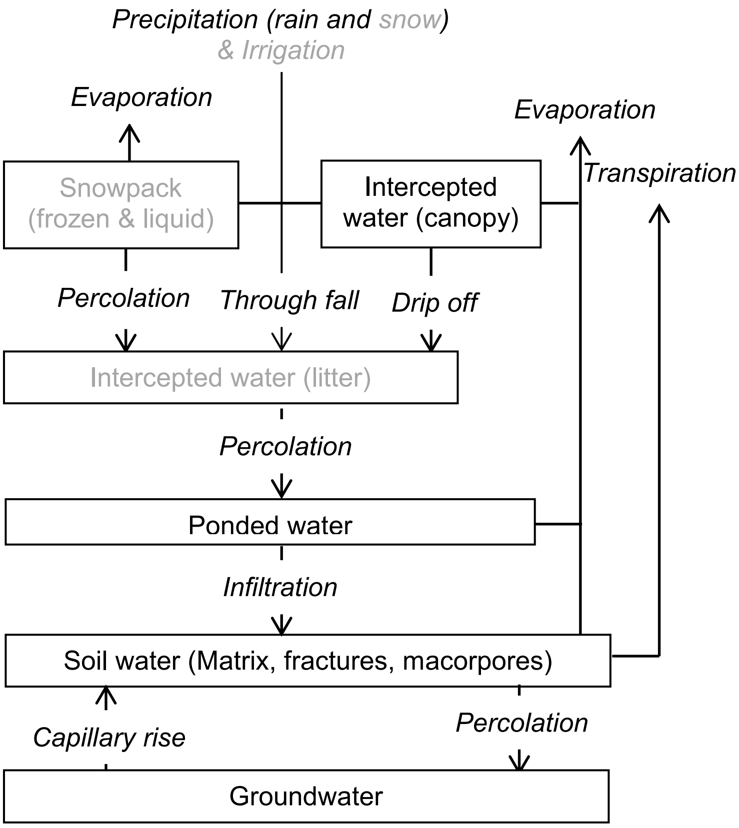

Figure 3: Modified schematic overview of the water balance DAISY according to Hansen et al. (2012a). Snow- and irrigation- precipitation, the snowpack and the interecepted water on the litter are omitted in the current study (greyish colored).

The soil water regime in the matrix is described by a numerical solution according to the Richard equation, and the flow is described by the Darcy's law (Abrahamsen, 2011). According to Hansen et al. (2012) through-fall, interception capacity, the transpiration of the leaves and the soil evaporation (directly connected to soil water content) depend all on the LAI. Furthermore the surface water storage, important for the initiation of preferential flow, is only activated when the water input (through fall, percolation and drip off) is bigger than the infiltration capacity of the soil surface Hansen et al. (2012). Therefore, the macropores and their emptying rate are dependent on the receiving water rate of the soil. If the macropore is directly connected to a subsurface drain, the emptying is instantaneous. The water extraction from roots to the atmosphere is dependent on the root density and the gradient in soil water pressure potential (governs water flow) between root surface and bulk soil (Hansen et al., 2012a). The modelled evapotranspiration is based on the energy balance of the surface. For further details refer to Hansen (2002) and Hansen et al. (2012a).

1.3.2 Agro- chemicals (solute balance)

Figure 4 points out the main processes a pesticide follows through the simulations. The solute balance is divided into surface balance and soil solute balance (Abrahamsen, 2002). Artemisinin is exclusively deposited on the soil directly and not additionally on the leaves.

Therefore the washing off and dissipation factor is neglected. As well surface runoff is ignored because the assumption has been made that both study fields have a flat topography. The same is true for colloid facilitated transport which accounts DAISY only with clay particles, released as a result of the impact of rain drops on the soil surface (Abrahamen, unpublished). As artemisinin is partitioning mainly to organic matter, no clay sorption is assumed and therefore the transport on soil colloids are not further traced. Lastly, plant uptake Artemisia annua have been so far not observed (Hermann et al., 2012).

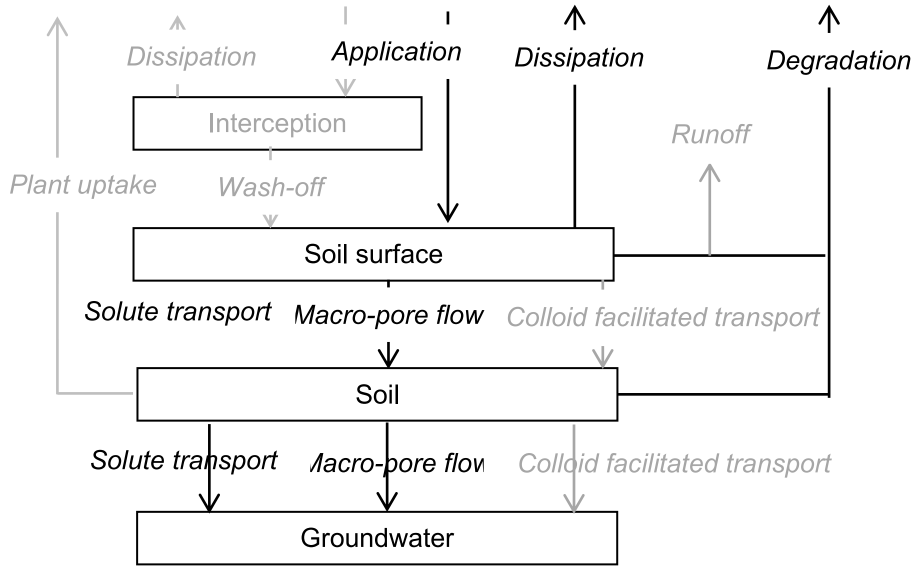

Figure 4: Modified schematic overview of the pesticide fate model according to Hansen et al. (2012a). Dissipation, the applicated chemical compound intercepting, the wash- off from the leaves, both colloid facilitated transport, the surface leaching and the plant uptake are omitted in the current study (greyish coloured).

In the soil system, artemisinin is exposed to sorption, degradation and transport (Hansen et al., 2012a). Degradation is described by first-order kinetics and depends on the temperature, moisture, and soil depth. Sorption is supposed to be instantaneous (at the equilibrium stage) and is characterized in this case by the Freundlich isotherms (i.e. K_F) and adjusted to the carbon content (i.e. K_{FOC}) (Hansen, 2002). The solute balance model is based on the convection –dispersion equation and is only valid when local equilibrium is obtained which is the case when no preferential flow takes place (Abrahamsen, 2002). As in the sandy loam soil preferential flow is modelled; DAISY follows a second flow regime in the macropores where only convection is considered. According to Abrahamsen (2002), exchange between matrix flow and the preferential flow is a sink-source term incorporated in the convection-dispersion equation and is governed by the water flow. There is no storage in macropores considered. For more information refer to Hansen et al. (2012a) and Abrahamsen (2002).

1.3.3 Plant growth

Instead of modelling the specific growth and realising pattern of Artemisia annua, the predefined ‘permanent grass’ vegetation type of the DAISY library was used (see Abrahamsen, 2103). It includes important default factors such as potential evapotranspiration, interception capacity, a static reflection factor (albedo), and permanent root depth of 30 cm. Therefore, only important factors influencing the water balance in the soils were chosen and plant growth modelling procedure with flows of matters such as the partitioning of the assimilated carbon to the storage organs, leaves, roots and stems (Hansen et al., 2012a) are not included. The canopy structure is influenced by a daily changing LAI and the development stage, predefined values which are quantifying the physiological age in relation to the morphological appearance (‘emergence’, ‘flowering’ and ‘maturation’) (Hansen 2002 and Hansen et al., 2012).

Further processes which are incorporated in DAISY such as soil heat, carbon turnover (e.g. soil organic matter turnover) and nitrogen processes (e.g. nitrification, leaching, mineralization and immobilization) are neglected in the present study.

2 Material and Methods

2.1 Site description

Two representative agricultural soils from Denmark were chosen. One is a sandy soil from Jyndevad, southern Jutland, Denmark (N 55°2′ E 9°26′ / 16 meter above sea level) developed on glaciofluvial material from Weichselian glaciation and used for agriculture purposes. The topography is considered to be flat, erosion is not occurring, and the yearly average precipitation is 960 mm.

The soil from Taastrup, eastern Zealand, Denmark (N 55°40‘ E 12°17‘ / 25 meter above sea level) is used for agriculture purposes, has a yearly average precipitation of 600 mm and an average soil temperature of 8.3 °C. The landform configuration is almost flat with a slope of <2 % and imply moraine material from the Weichsel glacial period. Moreover, there is no erosion observed and the soil is well- drained.

Table 2: Selected soil properties for the sandy soil (Jyndevad) and sandy loam soil (Taastrup).

Geographical region	Soil type[a]	Horizon	Depth (cm)	Clay (%)	Silt (%)	Sand (%)	SOM (%)	ρ (g/cm^3)	Fe$_{ox}$[b] %	Al$_{ox}$[b] %	Fe$_{CBD}$[c] %	Al$_{CBD}$[c] %
Jyndevad	Sand	Ap	-30	3.8	7.2	86.7	2.3	1.47	0.16	0.08	0.31	0.10
	Sand	C	-250	2.8	2.3	94.5	1.4	1.47	-	-	-	-
Taastrup	Sandy loam	Ap	-25	10.7	22.2	67.1	3	1.49	0.26	0.08	0.61	0.08
	Sandy loam	Plow pan	-33	14.8	21.4	63.8	1.6	1.70	0.20	0.09	0.75	0.10
	Sandy clay loam	Bt	-120	22.2	19.5	58.3	1.6	1.65	0.17	0.08	0.83	0.10
	Sandy clay loam	C	-200	20.7	23.5	55.8	1	1.69	0.08	0.05	0.65	0.06

[a] Determined by the USDA soil texture triangle (see appendix I)
[b] Oxalate-extractable Fe and Al
[c] Citrate- bicarbonate-dithionite extractable Fe and Al.

2.2 Sorption and quantification of artemisinin

2.2.1 Chemicals

The chemicals used for the sorption batch experiment were Ethanol (96%) and Acetone which were purchased from Kemethyl (Køge, Denmark) and VWR International (Haasrode, Belgium), respectively. Artemisinin (98% purity) was provided by Sigma Aldrich (Brønsby, Denmark). For the subsequent extraction, determination and quantification methods Methanol and Acetonitrile were purchased from Rathburn Chemicals Ltd. (Walkerburn, Scotland), Na_2HPO_4 and NaH_2PO_4 from Merck (Darmstadt, Germany), Sodium hydroxide

(NaOH) and Acetic acid from J.T. Baker (Herlev, Denmark). Ethyalacetate and Hexane were both purchased from Merck (Darmstadt,Germany).

2.2.2 Sorption batch equilibrium procedure

Adsorption and desorption experiments were carried out according to the OECD (2000) guidelines. The direct method was applied which states that both artemisinin dissolved in the soil solution (supernatant) and the artemisinin sorbed to the soil matrix were determined. The air dried soil samples were sieved through a 2- mm wide mesh and afterwards 2.50 g measured and added into a 50 ml, round- bottomed, centrifuge glass tube (Hounisen, Laboriatorieudstryr, Risskov, Denmark) (Ap and C horizon for the sandy soil and Ap and Bt horizon for the sandy loam soil). Subsequently, 10 mL of deionized water was added to the centrifuge glasses and agitated overhead in the table-shaker at 16 rotations min^{-1} (Heidolph Reax 20) for about 12 hours in order to equilibrate the soil matrix with water. In the meantime, five different artemisinin stock solutions were set up with concentrations of 50, 40, 30, 20 and 10 µg mL^{-1} where the artemisinin powder got first dissolved in 1 % acetone and then filled up with deionized water in glass bottles. With a stirrer the mixtures were agitated and for two hours left open in order to evaporate the acetone. As a next step, 2.5 mL of the different stock solutions were added to the centrifuge glasses in order to get a soil/solution ratio of 1:5 (see appendix II), shaken overhead at 16 rotations min^{-1} in a table shaker for 4 hours and centrifuged for 10 min at 3000 rpm (ca. 800 Relative centrifugal force g) in a table centrifuge (Hettich Zentrifugen, Universal 30F). The sorption equilibrium time has been determined to be 4 hours and is elaborated in the appendix III. For each concentration and soil type triplicates were conducted and control samples without the soil but only the added concentration were placed aside. Furthermore, a blank run in duplicates, without artemisinin but with the same matrix/solution ratio of 1:5 was subject to the same procedure and was set up to detect interfering compounds or contaminated soil samples (OECD, 2000).

2.2.3 Extraction of artemisinin from soil solution

The following procedure is according to Jessing et al. (2009b). The supernatant was transferred to a 25 mL glass vial and added to a separation funnel. 6.25 mL of a ethyalacetate:hexane (50:50) solution was applied, hand-shaken and the organic phase tapped out. This extraction procedure was repeated once and afterwards the organic phase extract evaporated to complete dryness under a constant N_2 gas flow. The dry extracts were dissolved in 1.00 mL ethanol and stored cold.

2.2.4 Extraction of artemisinin from soil matrix

The following procedure is according to Jessing et al. (2009b). The separated soil matrix in the centrifuge glasses was mixed with 12.5 mL of ethanol, agitated in the table shaker for 24 hours and centrifuged for 10 min at 3000 rpm (ca. 800 Relative centrifugal force g). The supernatant was filtered quantitatively through a 20- to 25mm Whatmann 41 filter (Schleicher and Schuell, Keene, NH, USA) into a 25 mL glass vials. As above, the filtered supernatant was evaporated to complete dryness under constant N_2 gas flow, subsequently dissolved in 1.00 mL ethanol and stored cold.

2.2.5 Quantification and determination of artemisinin

Quantification and determination of artemisinin was conducted according to Jessing et al. (2009b), Zhao and Zeng (1985) and Qian et al. (2007) where the mentioned chemical compound got converted to the strongly UV- absorbing compound Q260 by a pre-column reaction (schematic diagrams see appendix IV). The dissolved extracts from the soil matrix and the soil solution are mixed up with 4 mL 0.2% (w/v) of NaOH (sodium hydroxide), heated up to 50˚C for 30 min and then again cooled down to room temperature. This solution was then acidified with 5 mL of 0.08 M acetic acid and filtered through a Millipore filter (0.45 µm) into the HPLC vials (Jessing et al., 2009b). The samples were measured with a HPLC (Agilent 1100 series) and separated in a Supelco Discovery Bio C18 Bio Wide Pore column (25 cm * 4.6 mm, 5 µm) (Sigma-Aldrich) with a temperature of 25˚C. The corresponding eluent (mobile phase) was methanol/acetonitrile/0.9 mM Na_2HPO_4- 3.6mM NaH_2PO_4 buffer (pH 7.76) solution (45/10/45 v/v) and the injection volume was 20 µL. The eluent flow was set to 1 mL min^{-1} and the detection value at a wavelength of 260 nm (Jessing et al., 2009b). Artemisinin has approximately a retention time of 5 min (see appendix IV).

2.2.6 The limit of detection (LOD) and limit of quantification (LOQ)

The estimation of the LOD and LOQ, based on the method of Boqué and Heyden (2009) and modified by Jessing et al (2009b), is three times standard deviation of ten samples with a concentration of three times the assumed LOD (according to Hermann et al. (2012) 0.053 µg mL^{-1}). The LOQ was determined as ten times the standard deviation (see appendix V).

2.2.7 Calculations

According to the OECD (2000) the Freundlich sorption isotherm equation relates the amount of test substance adsorbed to the concentration of the test substance in solution at equilibrium:

Equation 1: $C^{ads}_{s}\ (eq)\ (\mu g\ g^{-1}) = K^{ads}_{F} * C^{ads}_{aq}\ (eq)^{1/n}$

or in the linear form:

Equation 2: $\log C^{ads}_{s}\,(eq) = \log K^{ads}_{F} + 1/n * \log C^{ads}_{aq}\,(eq)$

where C^{ads}_{s} (eq) is the sorbed artemisinin concentration at equilibrium, K^{ads}_{F} the Freundlich sorption coefficient, n the regression coefficient, and C^{ads}_{aq} (eq) and the artemisinin concentration in solution at equilibrium.

According to OECD (2000) the organic carbon normalized Freundlich sorption coefficient K_{FOC} relates to the Freundlich sorption isotherm K_F and to the content of the organic sample in the soil sample:

Equation 3: $K_{FOC} = K_F * 100 / \%oc$

According to OECD (2000) the mass balance (MB) is defined as the percentage of substance which can be analytically recovered after an adsorption test versus the nominal amount of substance at the beginning of the test:

Equation 4: $MB = ((m^{ads}_{s}\,(eq) + m^{ads}_{aq}\,(eq)) * 100) / m_o$

where m^{ads}_{s} is the mass of artemisinin sorbed to the matrix at equilibrium, m^{ads}_{aq} the mass of artemisinin in solution at equilibrium and m_o the initial mass added to the soil sample.

Standard error of the mean:

Equation 5: $SEM = s / \sqrt{n}$

where s is the standard deviation and n is the sample size

In order to calculate the artemisinin concentration in the upper groundwater following assumptions have been taken:

Equation 6: *Leaching concentration upper groundwater (g* m^{-3} *or mg* L^{-1}*) = leaching content above groundwater (g* ha^{-1} $year^{-1}$*) / annual percolation above groundwater (*m^3 ha^{-1} $year^{-1}$*)*

for each year the annual sum of the leaching content and the percolation is calculated. In DAISY the annual percolation is denoted as ‘mm’ which equals 10 times ‘m^3 ha^{-1}’

2.3 DAISY model parameterisation

2.3.1 Basic scenario

The DAISY manager model and the DAISY input language is described in Hansen et al. (2012), Abrahamsen (2011), and Abrahamsen et al. (2013) where all the necessary files can be downloaded. The most important input data are stated in this chapter. For a detailed description of the simulation set- up refer to appendix XIV and XV.

Soil properties

The same soil types were used as in the sorption batch experiment for artemisinin (see chapter 2.1). Additionally, physical soil properties were enlisted for DAISY and illustrated in table 3.

Table 3: Selected physical soil properties for the different soil types and horizons. The soil water hydraulics of the sandy soil are calculated by Brooks and Corey retention curve with Burdine theory. For the sandy loam soil the physical properties are corresponding to the van Genuchten retention curve with the Mualem theory (Abrahamsen, 2013).

Geograph. region	Soil type	Horizon	Theta_res[a]	Theta_sat[b]	n[c]	l[d]	α[e] (cm^{-1})	λ[f]	h_b (cm)[g]	K_sat (cm/h)[h]
Jyndevad	Sandy	Ap	0.036	0.435	-	-	-	0.446	-8.4	24.34
	Sandy	C	0.017	0.443	-	-	-	0.687	-8.7	64.08
Taastrup	Sandy loam	Ap	default	default	default	default	default	-	-	$1.74*10^{-1}$
	Sandy loam	Plow pan	default	0.3394	1.1939	-2.9295	0.0475	-	-	$4.63*10^{-2}$
	Sandy clay loam	Bt	default	0.3570	1.1477	-4.0323	0.0565	-	-	$2.67*10^{-1}$
	Sandy clay loam	C	default	0.3483	1.1534	-3.6032	0.0476	-	-	1.50

[a] Soil residual water content (Default 0)
[b] Saturation point (fraction)
[c] van Genuchten n (dimensionless) (default 2)
[d] tortuosity parameter (dimensionsless) (default 2)
[e] van Genuchten alpha
[f] lampda (dimensionsless), pore size index
[g] bubbling pressure
[h] Water conductivity of saturated soil

Input files

Several input files according to Abrahamsen et al. (2013) were added to the simulation set-up and subsequently applied during the simulation procedure:

- ‘vegetation.dai‘. *Artemisia annua* L. was simulated as a permanent grass with a static root zone, no root uptake was considered and annual LAI was adapted according to table 4.

Table 4: Annual LAI pattern adapted to the Julian calendar

	Julian day	LAI
Emergence	147	0.0
Start of fast growth	224	1.0
Full canopy	315	5.0
Harvesting	322	0.0

- ‘chemistry-base.dai‘
- ‘dk-soil.dai‘
- ‘log.dai’

Soil sorption properties

Sorption properties of artemisinin for both soils origin from the current study and are stated in table 5. The K_{FOC} and 1/n for each horizon of the sandy soil and sandy loam soil were merged together to one value per soil type.

Table 5: Artemisinin sorption properties for both soil types. The K_{FOC} and 1/n values were experimentally determined in the present study (see appendix X.I)

	Sandy soil	Sandy loam soil
K_{FOC}[a] ((mg L^{-1})$^{-m}$)	41.94	32.92
1/n[b]	0.45	0.59

[a] In DAISY stated as ‘K_{OC}‘
[b] In DAISY stated as ‘m’ (dimensionless)

Soil degradation properties

Degradation properties are according to Jessing et al. (2009b) and are stated in table 6.

Table 6: Degradation values for artemisinin in the sandy and sandy loam soil according to Jessing et al. (2009b).

	Sandy soil[a,b]	Sandy loam soil[b]
Half-live DT50 (days)	13.5	8.3

[a] same sandy soil from the Jyndevad region
[b] for more information about the soil properties see Jessing et al. (2009b)

Artemisinin degradation is a function of soil depth and table 7 lists the factors according to FOCUS (2002).

Table 7: Decompose_depth_factors according to FOCUS (2002)

Soil depth (cm)	Factor
-95	0.3
-65	0.3
-55	0.5
-35	0.5
-25	1.0
0	1.0

Weather data

- Geographical region: Jyndevad (sandy soil). Weather data file according to Abrahamsen et al. (2013): 'dk-taastrup-hourly.dwf'. Additionally, inclusion of up-scaling factor of the precipitation scale to Jyndevad- weather condition according to table 8. In appendix

Table 8: Up-scaling factors of the precipitation pattern for the 'dk-taastrup-hourly.dwf'-file. Used for the Jyndevad region.

	Jan	**Feb.**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Oct**	**Nov**	**Dec**
Factor	2.19	1.96	1.21	1.22	1.28	1.36	1.29	1.14	1.80	1.66	2.09

- Geographical region: Taastrup (sandy loam soil). Weather data file according to Abrahamsen et al (2013): 'dk-taastrup-hourly.dwf'

Artemisinin load

The artemisinin load (g ha^{-1} day^{-1}) for the simulation set-up is according to Jessing et al. (2012a). Other than the single dose spraying in case of pesticides, the soil environment is exposed to continuous release of artemisinin. However, the measured loads of artemisinin are snapshots on a two weeks basis and the quantitative amount of artemisinin was up-scaled to 100'000 plants ha^{-1}. Furthermore, the artemisinin content in the experimental soil was measured in the upper 5 cm and origins from dead leave material, rain runoff and roots. For more information refer to Jessing et al. (2012a).

Start of release was assumed each year the 1th of June until the 1th of October where the plant got harvested, collected and removed instantly from the field. Table 9 exhibits the artemisinin load and the corresponding temporal pattern. For more information refer to appendix X.II.

Table 9: Artemisinin load within one year according to Jessing et al. (2012a). The flux density changes every two weeks and is based on the measured soil concentration from the upper 5 cm topsoil. Artemisinin is released at hour 1 every day.

Dates	**Age of plants (weeks)**	**Soil content (g ha^{-1})[a]**	**Artemisinin load (g ha^{-1} day^{-1})**
1th June	11	33.02	
15th June	13	58.72	1.8355
1th July	15	80.70	1.5699
15th July	17	123.11	3.0293
1th August	19	135.35	0.8748
15th August	21	145.97	0.7586
1th September	24	178.15	2.2985
15th September	26	185.85	0.5500
1th October	28	192.91	0.5037

[a] measured in the upper 5 cm topsoil.

Other parameters

Table 10: Important parameters for all scenarions of the simulation set- up.

Parameters	Sandy soil	Sandy loam soil
Groundwater Z_aquitard (cm)	250	200
Groundwater K_aquitard (cm/h)	-	0.050
Macropores (cm)	No[a]	until 150cm
Lateral drainage pipes (cm)	No	110
Colloid transport	No	No
Surface runoff	No[b]	No[b]

[a] there are macropores in the Ap- horizon. But due to constant bioturbation exposure there are no macropores considered.

[b] landform considered to be flat.

2.3.2 Scenario 1

For scenario 1 the DT50 for the loamy sand soil have was changed to 4.3 days (‘one-at-a-time-sensitivity analysis’). The new half-live was based on the soil degradation properties of the herbicide atrazine which has similar chemical properties than artemisinin. A degradation study on a sandy loam soil exhibit DT50 values between 6 and 14 days for atrazine (Food and Environment Protection Act, 1992). Therefore the DT50 was changed in this range. For more information refer to appendix X.III.

The DT50 for sandy soil was omitted because of the very low leaching concentration to the upper groundwater (see chapter 3.2.1), and the used DT50 of 13.1 days is rather high. The other parameters remained the same (see chapter 2.3.1).

2.3.3 Scenario 2

The second parameter that is subject to a simple ‘one-at-a-time-sensitivity analysis’ is the artemisinin load. A comparison to other studies is showing a much higher release from different cultivars and geographical regions. Janick and Ferreira (1996) stating that *A. annua* usually produces between 0.01% to 0.4% artemisinin of plant dry weight. According to Jessing et al. (2012a), the variety used in the current work produces on average 0.19%. Therefore the artemisinin load is doubled and stated in the appendix X.IV. The other parameters remained the same (see chapter 2.3.1).

3 Results

3.1 Freundlich sorption isotherms

The LOD was determined to be 0.43 µg mL^{-1} and the LOQ 1.43 µg mL^{-1}. According to table 11, the K_F- and K_{FOC}- values exhibited larger values for the Ap- horizons compared to the C- and Bt- horizon. Conversely, 1/n was considerably larger for the Bt- horizon than the Ap in the sandy loam soil whereas 1/n in the C- horizon was marginal larger than the Ap- horizon in the sandy soil (for more information refer to appendix VII.III).

Table 11: Parameters for the Freundlich adsorption isotherm and K_{FOC} of artemisinin for the sandy and sandy loam soil. They are based on the log-log sorption isotherm in figure 5 and 6.

	K_F	1/n	K_{FOC}	R^2
Sandy soil / Ap horizon	0.61	0.41	45.79	0.55
Sandy soil / C horizon	0.31	0.49	38.09	0.83
Sandy loam soil / Ap horizon	0.58	0.46	33.57	0.65
Sandy loam soil / Bt horizon	0.30	0.73	32.27	0.95

The Ap- horizon for the sandy soil in figure 5 showed a higher sorption capacity than the C horizon. The corresponding K_F values in table 11 exhibited the same pattern with an Ap horizon twice as high as the C horizon. The slope of both horizons demonstrated a very similar pattern and values (see table 11). The SEM (error bars) showed for each sampling points higher values for the amount sorbed to the soil matrix than for the amount in the soil solution. This is true for both horizons.

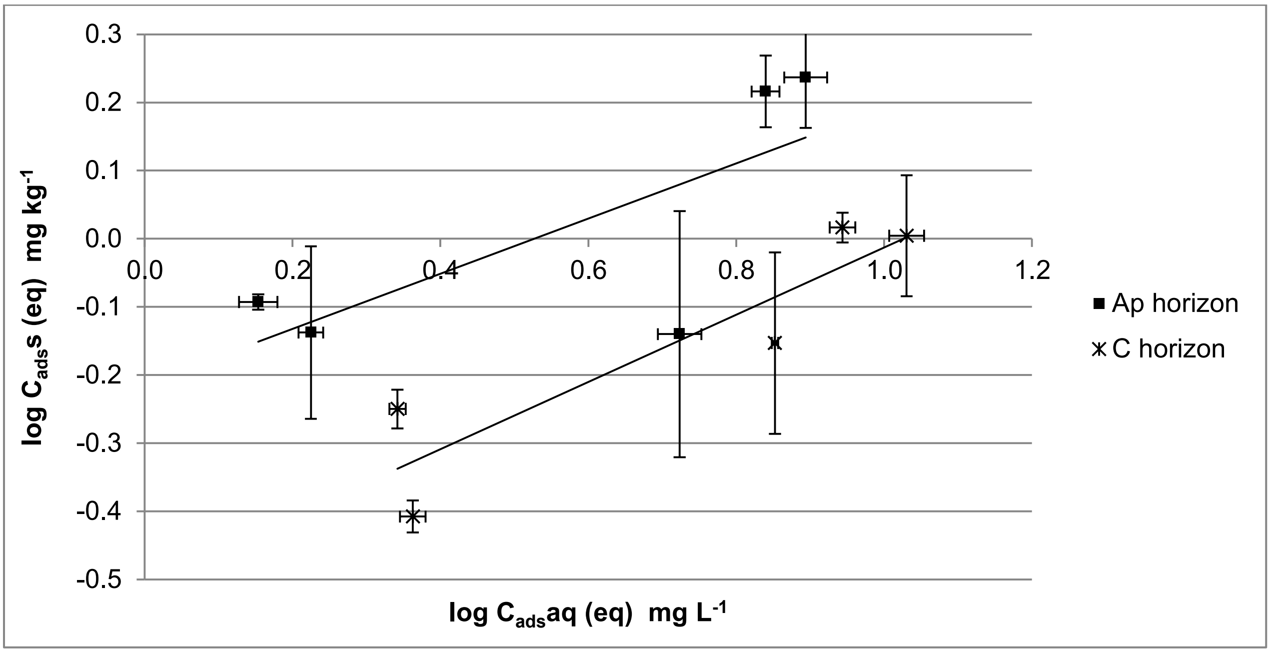

Figure 5: Linearized log-log Freundlich sorption isotherm of artemisinin in the sandy soil of the Ap and C horizon with its corresponding trendlines. The error bars are the calculated SEM of each samping point.

The Ap- horizon for the sandy loam soil in figure 6 exhibited a higher sorption capacity than the Bt- horizon. The corresponding K_F values presented the same pattern with an Ap horizon twice as high as the C horizon (see table 11). The slope (1/n) of the Bt- horizon revealed a larger value of 0.73 compared to the Ap- horizon of 0.46, which exhibited the steeper trendline for the Bt- horizon. The SEM values showed for each sampling points higher values for the amount sorbed to the soil matrix than for the amount in the soil solution. This is true for both horizons.

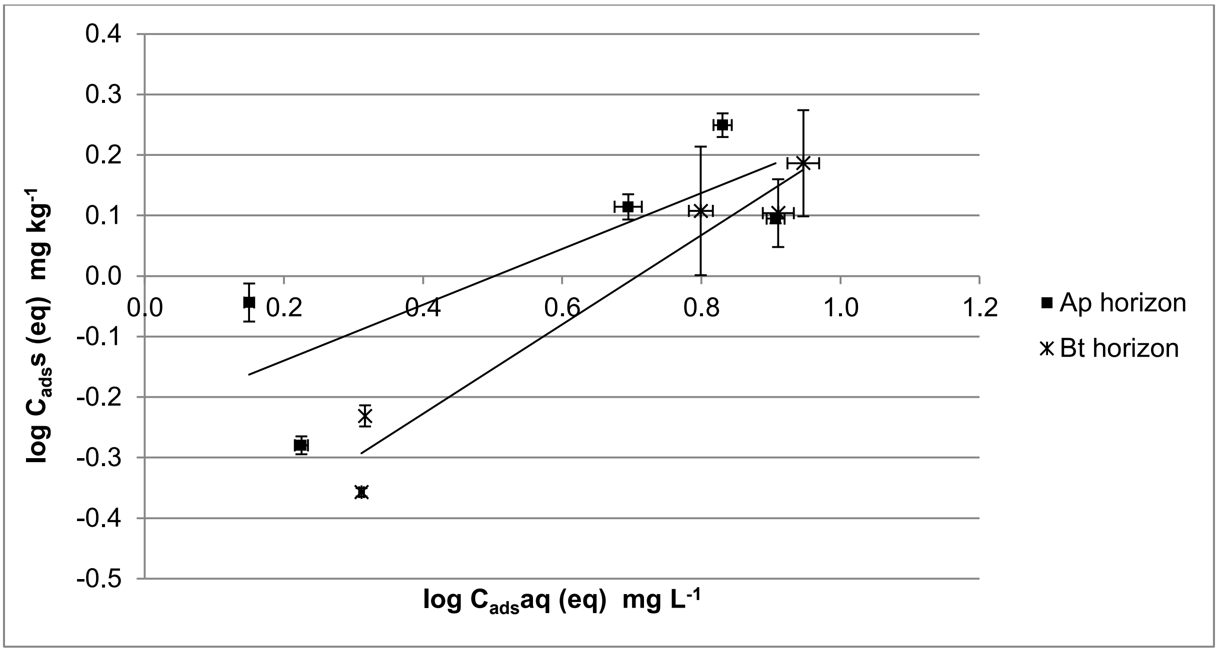

Figure 6 Linearized log-log Freundlich sorption isotherm of artemisinin in the sandy loam soil of the Ap and Bt horizon and the corresponding trendlines. The error bars are the calculated SEM of each samping point.

In figure 7, the non- linearized sorption isotherms revealed the highest sorption capacity for the Ap horizon of the sandy loam soil. The Ap- horizon of the sandy soil exhibited a similar capacity but the slope is less steep. The Bt- horizon exhibited the highest sorption intensity (steepest slope). At the highest solution concentration, both Ap- horizon and the Bt- horizon showed similar sorbed amount of artemisinin. The C- horizon of the sandy soil possessed the lowest capacity and intensity.

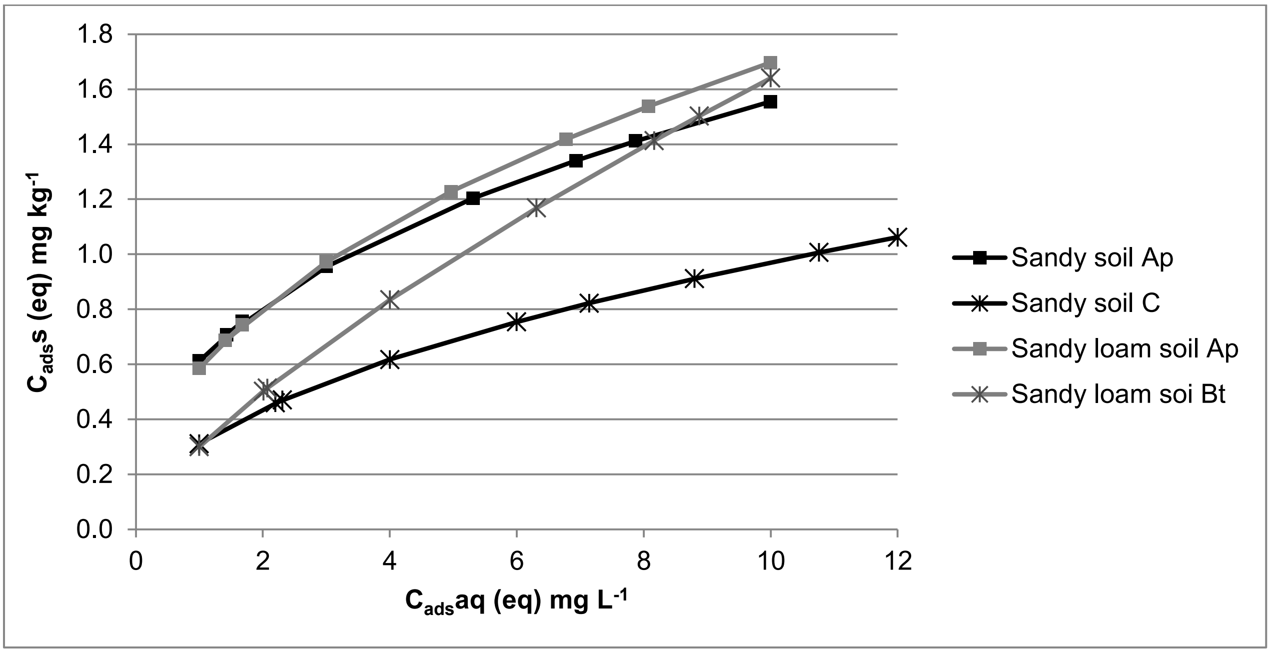

Figure 7: Non- linearized sorption isotherms, calculated according to equation 1 and with the corresponding K_F- and 1/n- values. The empirical coefficient K_F is modulated by the deviation from of the 1/n exponent for each horizon (Greenand and Karickhoff, 1990).

3.2 DAISY simulation- basic scenario

3.2.1 Sandy soil

Figure 8 shows the artemisinin balance in the whole sandy soil profile where all the infiltrating artemisinin got degraded each subsequent spring. No leaching occurred and therefore no content accumulation happened above the groundwater.

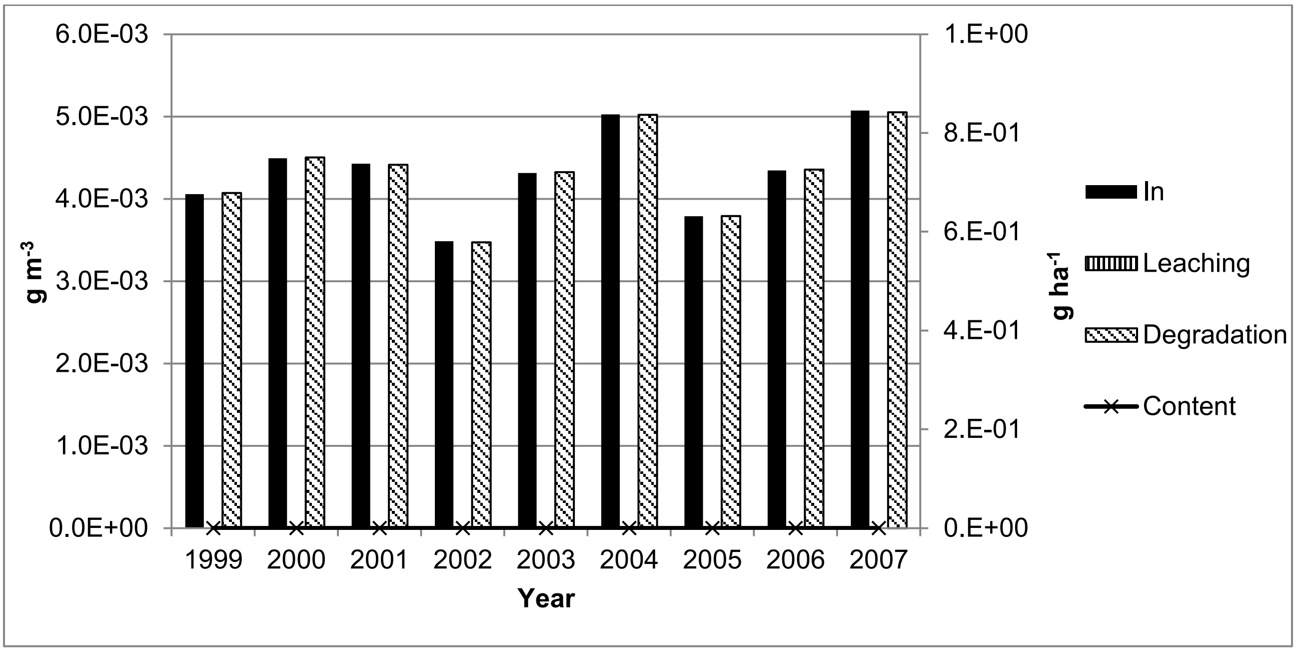

Figure 8: Artemisinin balance in the sandy soil within the whole soil profile (0- 250 cm) and all simulated years. It is consisting of the infiltrating concentration ('In'), leaching to 250 cm depth and degradation which are all annual concentration sums (primary vertical axis, concentration considered to be mass per volume soil system). The content is simulated on a daily snap-shot basis on the last day of each year (secondary vertical axis).

According to figure 9 all artemisinin got fully degraded until each subsequent winter or spring and was accumulated afresh on the 1st of June. An erratic fluctation, containing two peaks, was observed each year with the highest peak of around 29 g ha^{-1} in 250 cm soil depth in 2004.

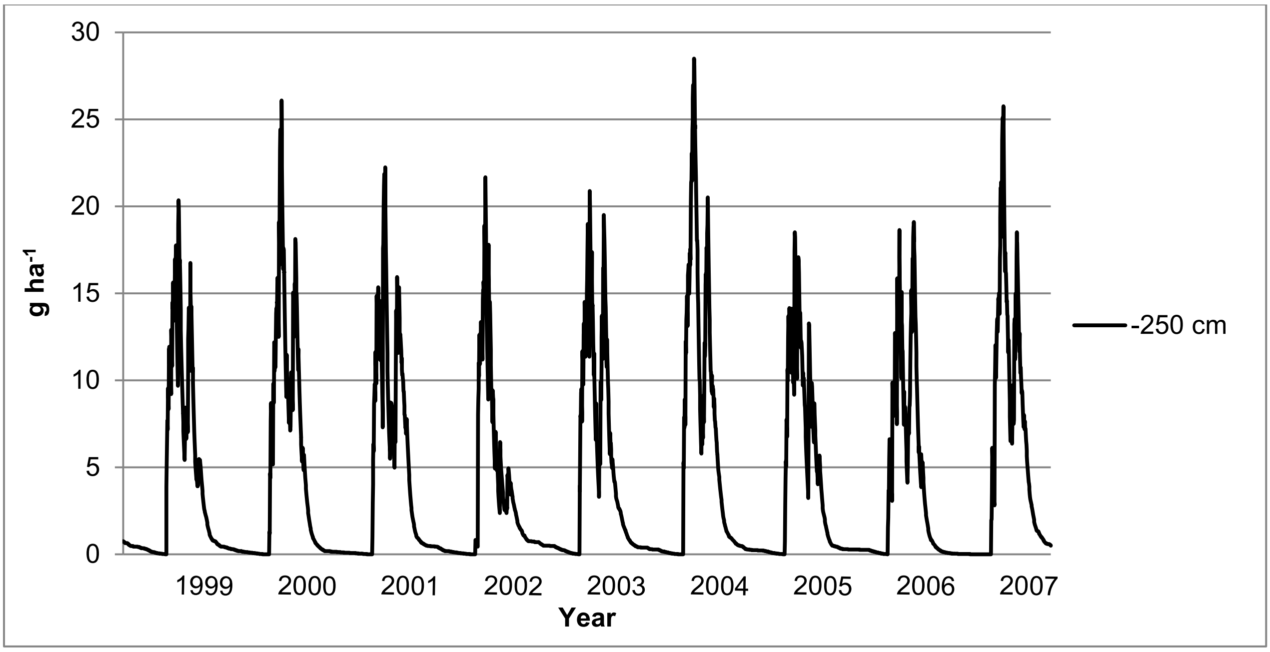

Figure 9: Artemisinin content trend for the basic scenario over the entire simulation period (1999- 2007) and the whole soil profile (0- 250 cm).

According to figure 10, the highest yearly leaching concentration (mass per volume soil system) in the sandy soil was with 4.2 * 10^{-14} g m^{-3} in 2007. This was observed in a depth of

100 cm depth and in the remaining years and depths, the leaching concentration ranged from 10^{-19} g m^{-3} until 10^{-20} g m^{-3} (considered to be zero).

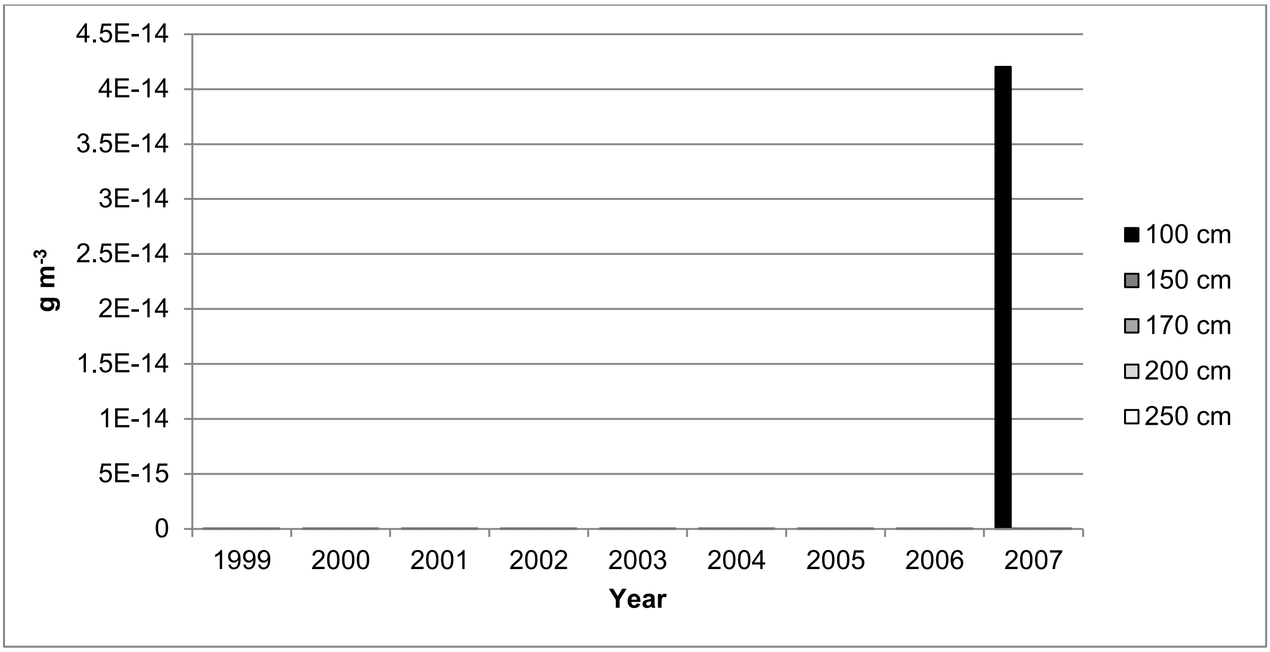

Figure 10: Artemisinin leaching concentration trend for the basic scenario within five different dephts in the sandy soil and over the whole simulation period (1999- 2007, concentration considered to be mass per volume soil system).

3.2.2 Sandy loam soil

Figure 11 shows the artemisinin balance in the whole sandy loam soil profile where most of the infiltrating artemisinin got degraded each subsequent spring. Although not visible, the leaching concentration increased in the whole soil profile (0- 200cm) from 3.3 * 10^{-18} g m^{-3} in 1999 to 5.8 * 10^{-7} g m^{-3} in 2007. The content accumulated with the highest peak of 26.9 g ha^{-1} in 2007 in 200 cm soil depth. Preferential flow as well occurred to a soil depth of 150 cm in irregular intervals ranging from the lowest concentration of 1.5 *10^{-5} g m^{-3} in 2002 to the highest peak of 2.4 *10^{-4} g m^{-3} in 2003. The same is true for drainage. Artemisinin purged to the next adjacent water body within a range between 6.2 * 10^{-10} g m^{-3} in 1999 and 1.6 * 10^{-6} g m^{-3} in 2007 (not visible).

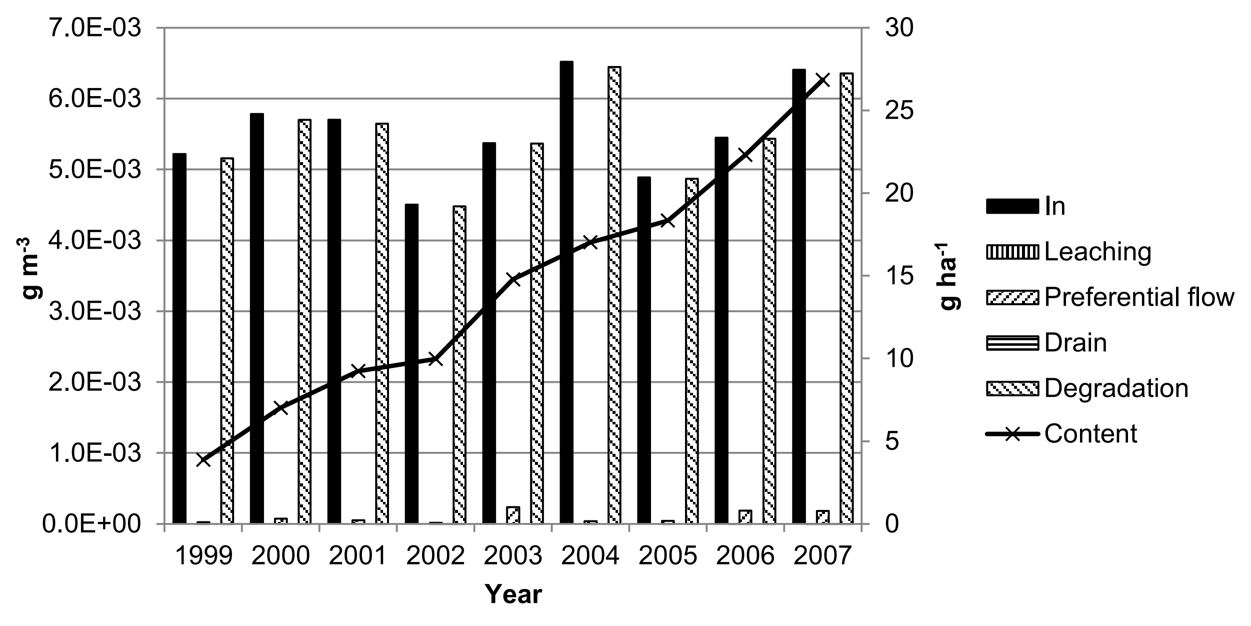

Figure 11: Concentration trend of artemisinin input and discharge in the sandy loam soil for the basic scenario within the whole soil profile (0- 200 cm) and all simulated years. It is consisting of the infiltrating concentration ('In'), leaching to 200 cm depth, preferential flow to 150 cm depth, drainage and degradation which are all annual concentration sums (primary vertical axis, concentration considered to be mass per volume soil system).The content is simulated on a daily snap-shot basis on the last day of each year (secondary vertical axis).

According to figure 12 all artemisinin got fully degraded from 0 to 100 cm depth until each subsequent spring and accumulated afresh on the 1st of June. In a soil depth from 100 cm to 200 cm artemisinin got accumulated. The accumulated content is made up of the difference between the trend- lines and the highest accumulated amount was observed 30 cm above the groundwater (170 to 200 cm) with 3.3 g ha^{-1} and occurs in the year 2007. Furthermore, an erratic fluctuation was observed each year with the highest peak in 2007 of about 45 g ha^{-1} in a depth range from 0 to 200 cm.

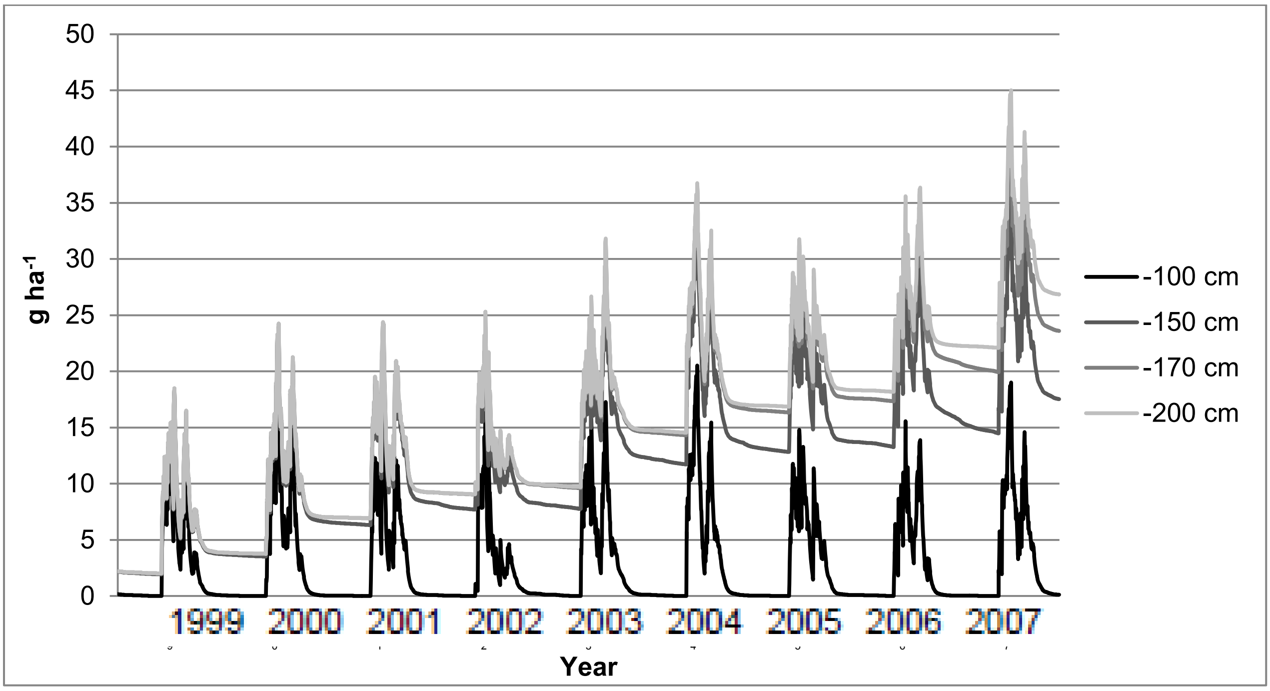

Figure 12: Artemisinin content trend in the sandy loam soil and the basic scenario over the whole measuring period (1999- 2007) and four different soil depths.

According to figure 13, the leaching concentration of each soil depth in the basic scenario was increased within the given time range. From 0 to 100 cm soil depth, the leaching concentration followed a fluctuating pattern from the lowest value of 2.8 * 10^{-7} g m^{-3} in 1999 to the highest of 4.1 * 10^{-6} g m^{-3} in 2007. In the soil depth from 0 to 150 cm the increased leaching concentration peaked highest in 2007 with a concentration of 2.0 * 10^{-4} g m^{-3}. However, in the soil depth between 0 and 200 cm the concentration ascended from 3.3 * 10^{-18} g m^{-3} in 1999 to 5.8 *10^{-7} g m^{-3} in 2007. Lastly, the leaching concentration caused by the preferential flow exhibited a fluctuating pattern with the highest concentration of 3.2 * 10^{-4} g m^{-3} in 2003.

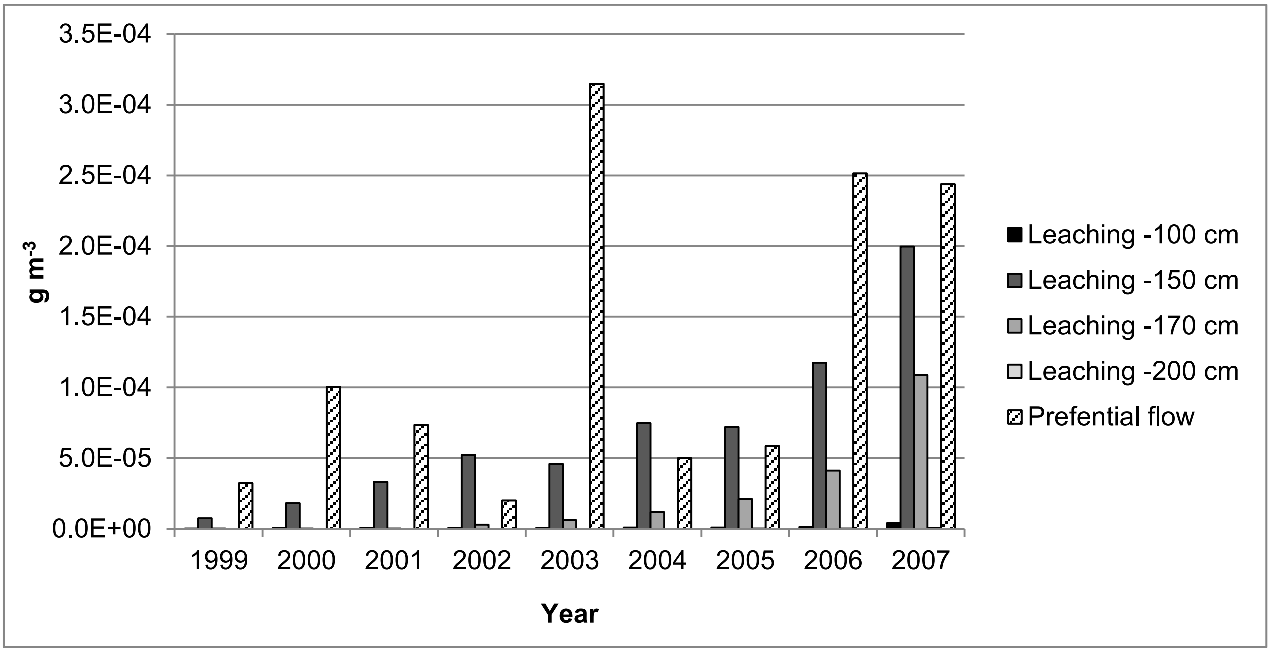

Figure 13: Artemisinin leaching concentration trend within four different soil depths in the sandy loam soil and over the whole simulation period (1999- 2007, average annual concentration). Prefential flow is as well included and is measured in a depth of 150 cm (average annual concentration).

Drainage of artemisinin in the sandy loam soil and the basic scenario is presented in figure 14 and revealed a fluctuating pattern. The drained concentration ranged from 1.1 * 10^{-10} g m^{-3} to 6.1 * 10^{-7} g m^{-3}, both in 2007.

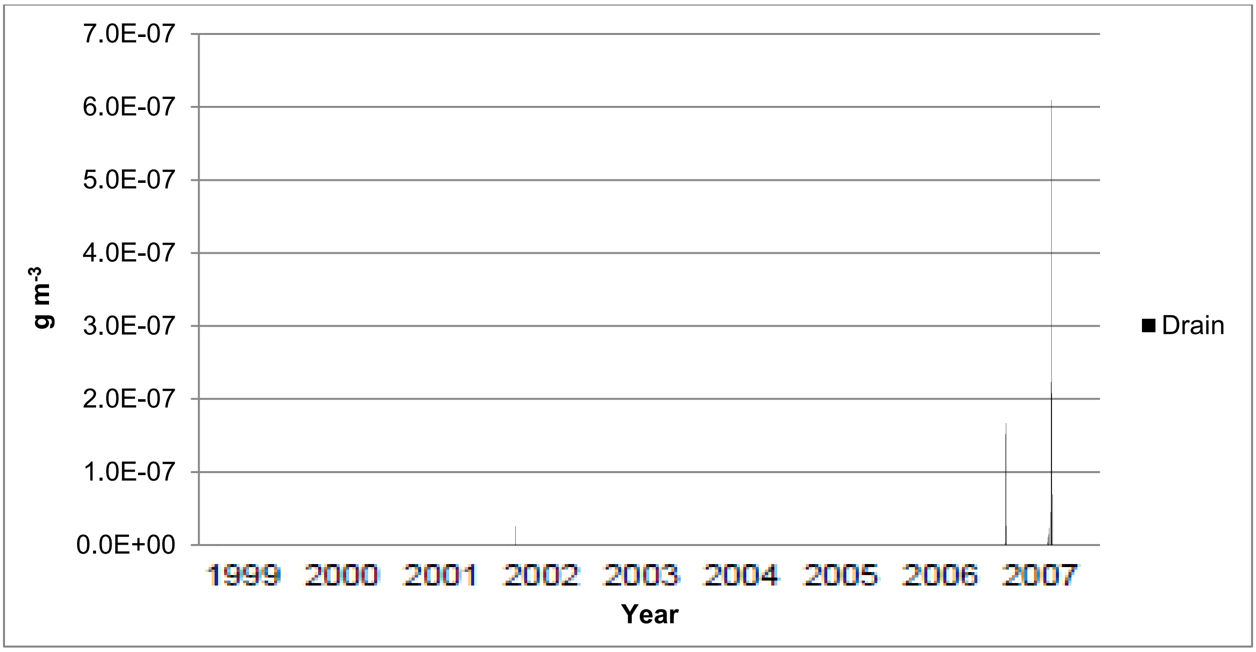

Figure 14: Drained artemisinin concentration over the whole simulation period (1999- 2007). The presented concentrations (mass per volume soil system) are daily snap-shots.

3.3 DAISY simulation- scenario 1

The comparison of the leaching concentration between the basic scenario (DT50 8.3 days) and scenario 1 (DT50 4.3 days) revealed a smaller concentration reaching the upper groundwater for scenario 1 (figure 15). During the whole simulation period, the leaching concentration for scenario 1 ended up in the upper groundwater increased from 1.35 * 10^{-18} g m^{-3} in 1999 to 3.7 * 10^{-8} g m^{-3} in 2007. For more results from scenario 1 refer to the appendix XII.

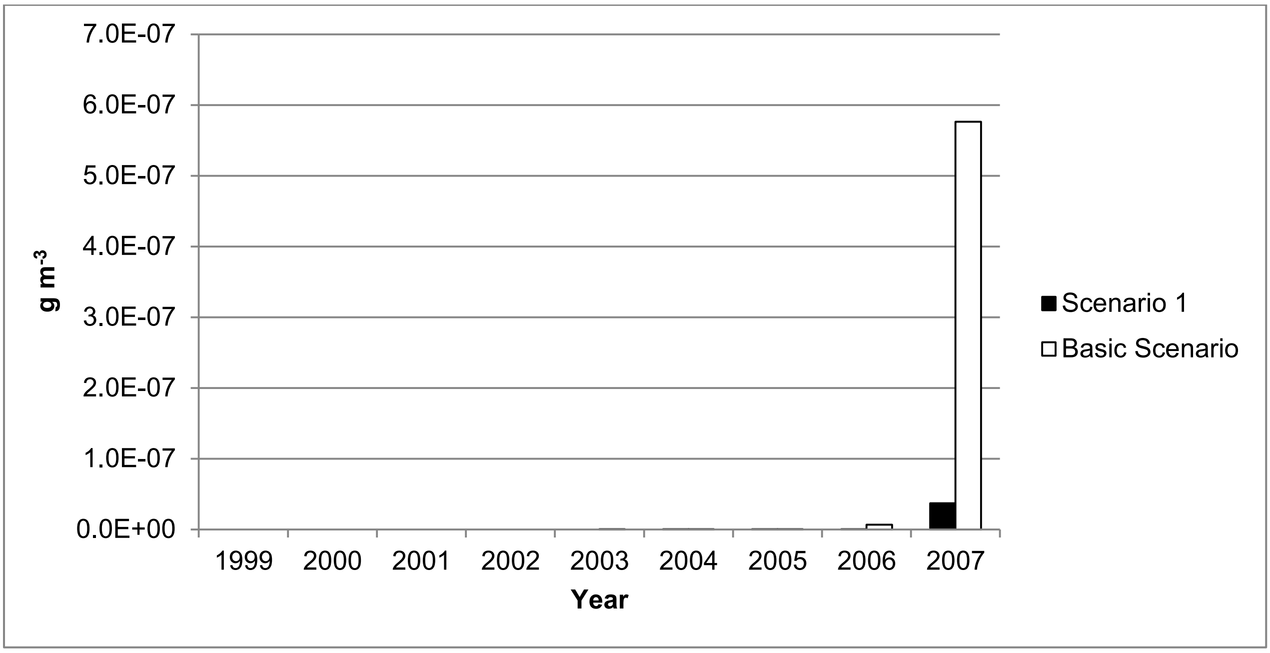

Figure 15: Artemisinin leaching concentration trend for scenario 1 and the basic scenario in the sandy loam soil, in depth range of 0-200 cm and over the whole simulation period (1999-2007, annual sums, concentration considered to be mass per volume soil system).

3.4 DAISY simulation – scenario 2

3.4.1 Sandy soil

According to figure 16, the highest yearly leaching concentration in the sandy soil in scenario 2 was with 1.95 * 10^{-13} g m^{-3} in 2007. That is in 100 cm depth and in the remaining years and depths the leaching concentration ranged from 10^{-18} g m^{-3} until 10^{-19} g m^{-3} (considered to be zero). For more results from scenario 2 refer to the appendix XIII.I.

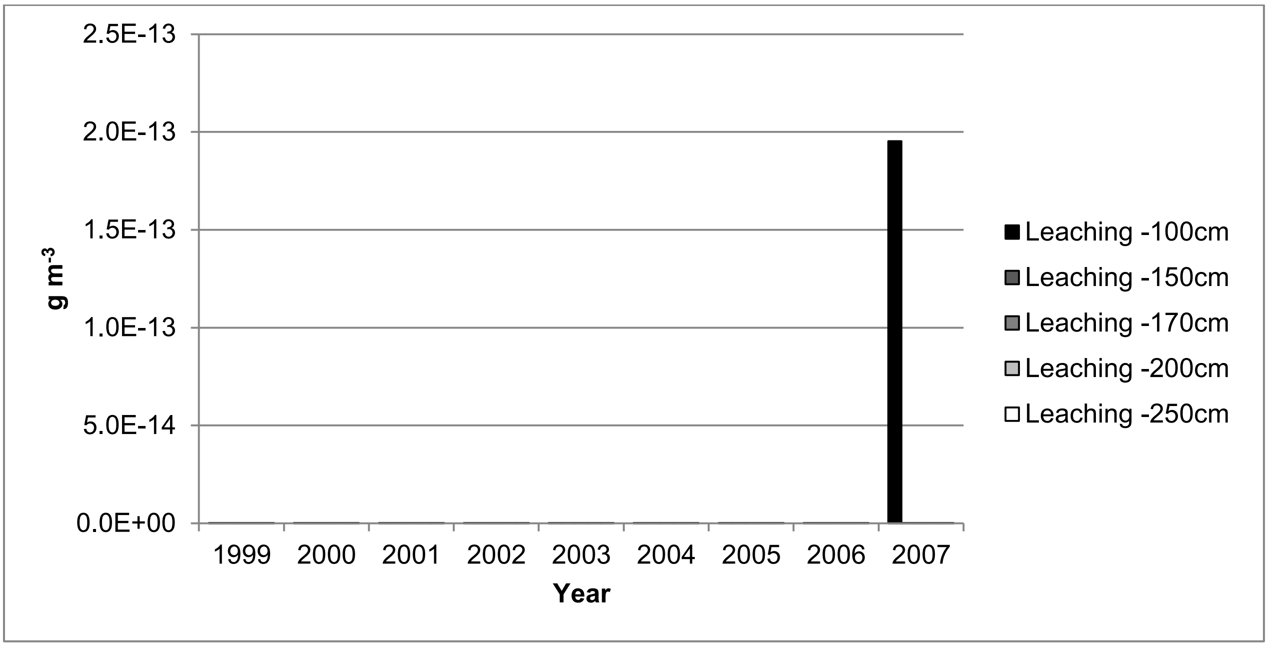

Figure 16: Artemisinin leaching concentration trend within five different dephts in the sandy soil for scenario 2 and over the whole simulation period (1999- 2007, concentration considered to be mass per volume soil system).

3.4.2 Sandy loam soil

According to figure 17, the leaching concentration of each soil depth increased within the given time range. From 0 to 100 cm soil depth the leaching concentration followed a fluctuating pattern from the lowest value of 1.18 * 10^{-6} g m^{-3} in 1999 to the highest of 1.55 * 10^{-5} g m^{-3} in 2007. In the soil depth from 0 to 150 cm the increased leaching concentration peaked highest in 2007 with a concentration of 5.5 * 10^{-4} g m^{-3}. In 170 cm depth it followed the same pattern with the highest peak in 2007 of about 4.1 * 10^{-4} g m^{-3}. In the soil depth between 0 and 200 cm the concentration ascended from 4.7 * 10^{-17} g m^{-3} in 1999 to 7.2 * 10^{-5} g m^{-3} in 2007. Lastly, the leaching concentration caused by the preferential flow exhibited a fluctuating pattern with the highest concentration of 6.2 * 10^{-4} g m^{-3} in 2003. For more results from scenario 2 refer to the appendix XIII.II.

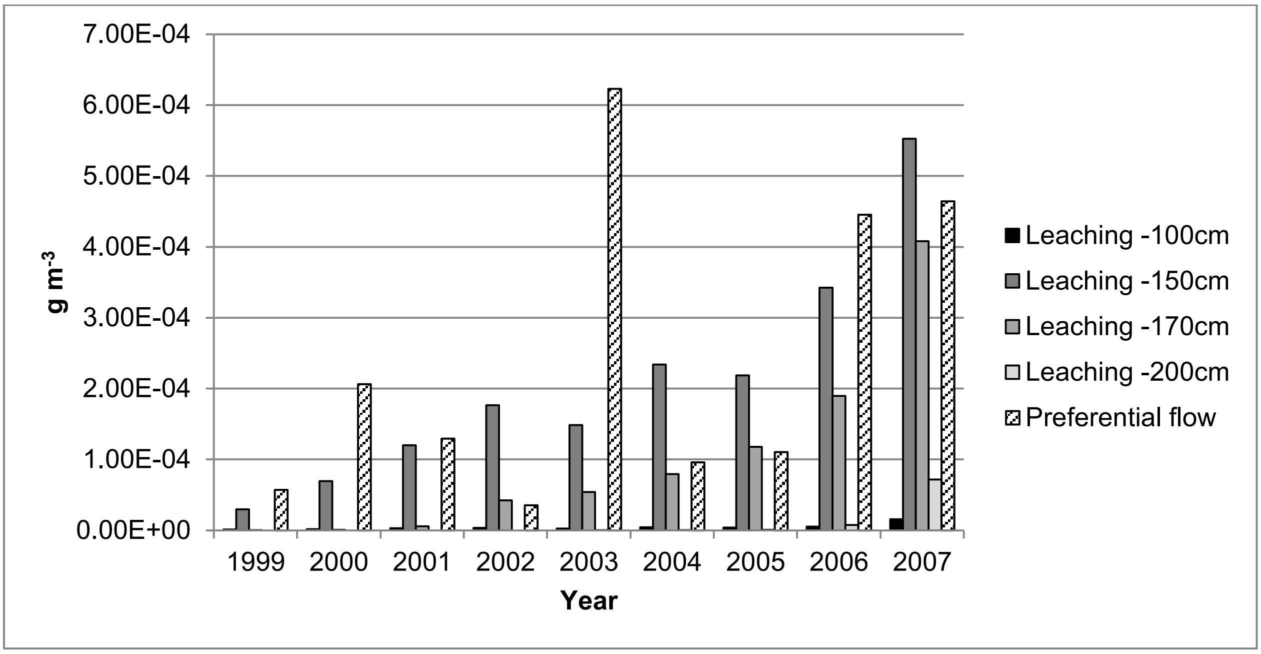

Figure 17: Artemisinin leaching concentration trend for scenario 2 within four different soil depths in the sandy loam soil and over the whole simulation period (1999- 2007, average annual concentrations). Prefential flow is as well included and is measured in a depth of 150 cm (average annual concentration, concentration considered to be mass per volume soil system).

3.5 Ecotoxicological assessment

Jessing et al. (2009a) calculated the concentration threshold of artemisinin that results in a 10 % (EC10) and 50 % (EC50) reduction in growth of freshwater algae (*Pseudokirchneriella sp.*) and duckweed (*Lemna minor*) (see table 12). The leaching- and drainage concentration and the accumulated content are calculated according to equation 6. It has to be stated that the freshwater algae and duckweed are not present in groundwater. However, groundwater is assumed to feed surface water bodies which will decrease the concentration tremendously due to dilution. Refer to appendix XIV for elaborated calculations.

Table 12: Ecotoxicological threshold EC10 and EC50 of artemisinin on freshwater algae (Pseudokirchneriella sp.) and duckweed (Lemna minor) according to Jessing et al. (2009a)

	EC10 (mg L^{-1})	**EC50 (mg L^{-1})**
Algae (*Pseudokirchneriella sp.)*	$1.6 * 10^{-1}$ +/-0.05	$2.4 * 10^{-1}$ +/-0.01
Duckweed (*Lemna minor*)	$2.6 * 10^{-2}$ +/-0.02	$1.9 * 10^{-1}$ +/-0.03

3.5.1 Basic scenario

Sandy soil

- No leaching considered due to numerical uncertainty.
- No accumulation simulated above the groundwater level

Therefore no exceedance of the ecotoxicological threshold according to table 12.

Sandy loam soil

- Highest leaching concentration reaching the upper groundwater is 2.13 * 10^{-6} g m^{-3} or **2.13 * 10^{-6} mg L^{-1}** 2007.
- Highest drained concentration is 2.68 * 10^{-4} g m^{-3} or **2.68 * 10^{-4} mg L^{-1}** in 2007.
- Continuous accumulation 30 cm above groundwater level attain 3.3 g ha^{-1} or **6.09 * 10^{-4} mg L^{-1}**

Therefore no exceedance of the ecotoxicological threshold according to table 12.

3.5.2 Scenario 1

Sandy loam soil

- Highest leaching concentration reaching the upper groundwater is 1.37 * 10^{-7} g m^{-3} or **1.37 * 10^{-7} mg L^{-1}** in 2007.
- Highest drained concentration is 1.71 * 10^{-4} g m^{-3} or **1.71 * 10^{-4} mg L^{-1}** in 2007.
- Continuous accumulation 30 cm above groundwater level attain 1.71 g ha^{-1} or **3.16 * 10^{-4} mg L^{-1}**

Therefore no exceedance of the ecotoxicological threshold according to table 12.

3.5.3 Scenario 2

Sandy soil

- No leaching considered due to numerical uncertainty.
- No accumulation simulated above the groundwater level

Therefore no exceedance of the ecotoxicological threshold according to table 12.

Sandy loam soil

- Highest leaching concentration reaching the upper groundwater is 2.64 * 10^{-4} g m^{-3} or **2.64 * 10^{-4} mg L^{-1}** in 2007.
- Highest concentration in the drainage is 9.5 * 10^{-4} g m^{-3} or **9.5 * 10^{-4} mg L^{-1}** 2007.
- Continuous accumulation 30 cm above groundwater level attain 13.6 g ha^{-1} or **2.51 * 10^{-3} mg L^{-1}**

Therefore no exceedance of the ecotoxicological threshold according to table 12.

4 Discussion

4.1 Sorption Experiments

4.1.1 Method evaluation

The low coefficient of determination (R^2), calculated from the linearized Freundlich- model, revealed uncertainty in the experimental outcome and the plotted data. Especially, the R^2 of both Ap-horizons can be criticised as having a low fitting degree for the plotted isotherm and kinetic models (Foo and Hameed, 2010) (see table 11). In the sandy soil, several sampling points in the Ap- horizon showed large error bars (i.e. high SEM) for the sorbed artemisinin and therefore caused the low R^2 (see figure 5). The C-horizon in the sandy soil exposes a better fitting degree, but also revealed larger error bars for the sorbed artemisinin than for the one in the soil solution. A similar pattern was seen for the Bt-horizon of the sandy loam soil as it exhibited high SEM-values in the sorbed artemisinin samples (see figure 6). One reason for the high SEM-values might be due to the low recovery values that soils with a higher organic content demonstrate (e.g. Ap- horizons). Hermann et al. (2012) and (Jessing et al. 2009b) are stating a recovery value of artemisinin on a humic soil to be 55%, whereas on sandy, clayey and loamy soils the recovery values are between 71 and 88%. The current recovery values range between 80 and 100% and the Ap-horizon of the sandy loam exhibited values in the lowest range (see appendix VI). The different recovery values point out the lower performance of the extraction method with ethanol on soil organic matter.
As the used soil samples are heterogeneous containing different organic matter contents, the recovery performances are different. According to Foo and Hameen (2010), the slope (1/n, range from 0 to 1) is a measure of surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. As especially both Ap-horizons and the C-horizon possess rather low 1/n-values, they can be considered as heterogeneous. Therefore, the recovery performance could be improved for soils with organic matter using a more effective extraction method and subsequently increasing the R^2 value.

There are other uncertainties involved in the applied method. According to OECD (2000), there are several parameters which could influence the accuracy of the sorption measurements and therefore the experimental performance of the test. For example the initial artemisinin concentration of 2 mg L^{-1} (actual 1.46 mg L^{-1}) and 4 mg L^{-1} (actual 2.76 mg L^{-1}), revealed a mass balance (MB) between 180 and 210% and 107 to 128%, respectively (see appendix VII.III). This could be explained with the measurement uncertainty that occur with concentration close to the LOD (0.43 mg L^{-1}). The OECD (2000) guideline states that the lowest concentration of the stock solution should preferably be two orders of magnitude higher than the LOD, which in the current case would be 43 mg L^{-1}. Therefore, it is recommended to raise the initial solution to a maximum concentration to that of the water solubility of artemisinin (50 mg L^{-1}) but not below a minimum concentration of 10 mg L^{-1}. The current results exhibited reasonable MBs above 10 mg L^{-1} and therefore this threshold would safeguard the ability to perform exact measurements (see appendix VII.III).

An additional suggestion from the OECD (2002) is the coverage of two magnitudes when setting up five different initial concentrations. However, to alter the magnitude of the solution concentration range would cause the above-mentioned implications with the LOD and water solubility and therefore the results of this work would rather recommend lowering the soil/solution ratio. Boesten (1994) is proposing a total sorbed percentage of > 50% and additionally with low K_F and K_d- values, a soil/solution ratio of 1:1 or 1:2. As the current K_F-values are low compared to other natural toxins and pesticides, the soil/solution ratio should be set in the proposed range.

Another factor, which could influence the accuracy of the sorption measurement, is the degree of instability of the substance during the experiment. A substance with a MB of less than 90 % can be considered as unstable (OECD, 2000), which applies partially for artemisinin in the highest initial concentration (14.1 mg L^{-1}) (see appendix VII.III). However, the study should still be continued, taking into account analysis of both the soil matrix and soil solution (direct method). The direct method is especially recommended for substances with weak sorption capacities, which is the case in the current study. In this way the quantitative degradation can be followed, which is important to consider when choosing the sorption equilibrium time. According to Hermann et al. (2012, oral note), no equilibrium times for the artemisinin sorption in their study were experimentally estimated, but nevertheless, the experiments were conducted within 2 hours. Conversely, in the current study the equilibrium time was set to 4 hours (see appendix III). After 2 hours sorption still occurred but until 24 hours the amount of sorbed artemisinin levelled off. Furthermore, fast degradation might influence the artemisinin concentration substantially within the first 24 hours in the solution and therefore the sorption process. This is proven by Jessing et al. (2009a), who measured a total degradation of 21.5 % of artemisinin in the sandy soil and 51.9 % in a loamy soil already after 24 hours. Moreover, Jessing et al. (2009b) proved that adsorption towards the used centrifuge tubes can be excluded.

Hence, the 4 hours equilibrium time is adequate, as it should not be raised because of the low MB of the highest initial concentration and it should not be decreased as sorption is still occurring.

Lastly, the mixing experiment of 24 hours may cause considerable aggregate breakdown, which should be considered since it might influence the sorption capacity of the soil matrix (Wauchope, 2002).

4.1.2 Artemisinin sorption

The Freundlich model is one of the most popular adsorption models for a single solute system and it is widely applied in heterogeneous systems especially those for organic compounds (Foo and Hameen, 2010 and Chilton et al., 2002). According to Wauchope et al. (2002), a log-log transformation, as it is completed with the Freundlich equation, will fit almost any sorption experiment data in soils. For both soils, the K_F-values got smaller with soil- depth (see table 11). This is indicating that artemisinin sorbs to organic matter, because the SOM in the soil is as well declining in respect to the depth (see table 2). Likewise shown in figures 5 and 6, the Ap-horizons exhibited quantitatively more sorbed artemisinin to the soil matrix than the corresponding horizon below. Furthermore, both Ap-horizons revealed very similar sorption behaviour, e.g. a comparable slope and K_F-value, although the texture is different (see figure 7). This illustrates again the major role of the organic matter. A similar pattern has been observed in a previous study with the same sandy loam soil where the sorption affinity decreased with increasing soil depth (Hermann et al., 2012). Furthermore, this pattern is in line with the calculated log K_{ow} of 2.9 (see table 1), which is expecting that artemisinin is sorbing mainly to the organic fraction, or in other words that partitioning (non-specific interactions) is the foremost sorption process (Hermann et al., 2012 and Jessing, 2012b).

Nevertheless, Hermann et al. (2012b) stated that artemisinin could likewise be sorbed via surface complexation. They identified a discrepancy between the actual measured K_d of 6.57 L kg^{-1} and the calculated K_d of 4.3 L kg^{-1}, based on the calculated K_{oc} (see table 1). As the measured K_d was higher, they assumed that artemisinin probably also sorbs through surface complexation on clay minerals. This hypothesis is supported by the present results. The Bt-horizon of the sandy loam soil exhibited the steepest slope, demonstrating a sorption type other than partitioning (see figure 7). According to Foo and Hameen (2010), the slope (1/n, range from 0 to 1) is a measure of sorption intensity. Both horizons of the sandy soil and the Ap- horizon of the sandy loam soil exhibited a flat slope of the linearized Freundlich isotherm. Thus, they all indicate low sorption intensity compared to the Bt- horizon of the sandy loam soil. And as the Bt-horizon possessed a larger clay content than the C-horizon (see table 2), artemisinin might sorb through surface complexation to clay minerals causing a higher intensity and reaching at higher solution concentration, the same amount of sorbed artemisinin than for both Ap-horizons (see figure 7). Clay minerals possess a much larger specific surface than primary minerals and as artemisinin is considered to be a non-ionic compound, the sorption might be caused by the means of hydrogen- or/and van der Walls bonds (Hillel, 1998). Further sorption processes can be neglected as artemisinin is lacking functional groups capable of binding to soil minerals (Jessing et al., 2009a).

The comparison between Bt- and C-horizon is important, because it can be assumed that surface complexation on clay particles might have only little effect on the soprtion processes of artemisinin except in soils with low organic matter which is the case in the mentioned horizons (Oepen et al., 1991).
However, if artemisinin sorbs to clay minerals by surface complexation, chemical degradation might occur as well. It is expected that Fe_{ox}, Al_{ox} and other metal-oxides could be responsible for the cleavage of the endoperoxide bridge of artemisinin and in this way, rather a chemical degradation than a sorption process would occur (Jessing, 2012). Desorption experiments could be carried out to prove to what extent either process takes place. In this way, potential degradation could be examined and whether or not artemisinin is fully reversible and therefore accessible for biological degradation.

The present sorption values are indicating for artemisinin a mobile behaviour in the soil according to PPDB (2013) and according to McCall et al. (1980) a high mobility. Wauchope et al. (2002) stated that any difference in the K_{FOC} of a factor of 10 or more can be considered as significant. Even though the C-horizon possesses the lowest K_{FOC}-value and is therefore mostly prone to leaching, the difference between the four horizons is not significant. The distribution coefficient K_d, K_{OC} and R^2 for the different horizons were also estimated and are illustrated with their corresponding diagrams in appendix VII.II. However, comparing both K_F and K_d and their corresponding K_{OC} and K_{FOC}, the Freundlich adsorption coefficient were the most appropriate. This was approved by the results of the root mean square error (RMSE) and the goodness of fit (see appendix IX). For this reason, and for the fact that artemisinin is partitioning mainly to the non- polar organic fraction the K_{FOC} will be incorporated in the DAISY simulation procedure.

4.2 DAISY simulation

4.2.1 Critical justification on parameterisation

The most important processes determining the leaching behaviour of artemisinin are degradation, sorption and desorption, uptake by the roots, volatilisation and the water balance in the atmosphere and soil (Van der Werf, 1996). In the current study, those processes were taken into account but the corresponding parameterisation depends on known chemical and physical properties of artemisinin, the local circumstances of both investigated sites, uncertainties, the availability of reliable data, expert's opinion, and the amount of work a modeller has to carry. As mentioned in the introduction, explanatory models such as the one applied in the current study attempt to generalize knowledge of natural toxins behaviour under field conditions by identification of the most important properties of the soil, the climate and the chemical compound (Boesten, 1999). This chapter critically states all the assumption made on the parameterisation of the simulation set- up, in order to justify the decisions but also to improve further simulation attempts.

As mentioned in the introduction, the releasing rate depends on various factors and varies usually between 0.01% to 0.4% artemisinin of plant dry weight (Janick and Ferreira, 1996) and up to 2 % (Meshnick et al., 1996). The variety used in the current work produces on average 0.19% which is considered to be relatively low (Jessing, 2012a). In order to embrace these differences, a sensitivity analysis was carried out (see chapter 4.2.2).

Once artemisinin is reaching the soil, it is partitioning either between the solid (i.e. soil matrix) or aqueous phase (i.e. soil solution). From there it can be washed off to the next stream or lake via runoff. The overflow might include artemisinin in its dissolved form, suspended particulate or as sediment- adsorbed on organic matter (Van der Werf, 1996). In the current work, runoff is not included due to the relatively flat topography. According to Jessing (2012b), artemisinin was found in the topsoil in various experiments one year after application. This persistency might cause surface- runoff and therefore should be continuously considered and if applicable, incorporated in the model.

Volatilization of the compound can be excluded because of the low Henry's law constant of $4.92 * 10^{-9}$ atm * m^3 mol^{-1} (Jessing et al., 2009a) and therefore as well its sorption of the vapour phase towards the soil matrix (Jessing et al., 2012b).

In respect of the artemisinin sorption (chapter 4.1), it is obvious that soil heterogeneity introduce uncertainty. According to Dubus (2003), spatial sorption variability was reported in a large number of geographical catchment areas (Barriuso and Calvet, 1992; Ahmad et al., 2001a; Dubus et al., 2001; Coquet, 2002), and on field and point scale (Jaynes et al., 1995;

Novak et al., 1997; Oliveira et al., 1999). Therefore this should be kept in mind when evaluating simulated results. As the organic content typically decreases with depth, sorption measurements for the subsoil are for artemisinin of importance. The current study merged the K_{FOC} of the top- and subsoil for each soil type for two reasons: firstly, they hold similar values (difference is not significant) and secondly the simulation with two separate K_{FOC} is simulation- wise laborious.

Degradation is described in DAISY by first order kinetics (Hansen et al., 2012). Beulke and Brown (2001) are claiming that models with first-order degradation have to be parameterised with degradation rates estimated by first- order kinetics, which is according to Jessing et al. (2009b) the case for the current used DT50. In the topsoil, degradation of artemisinin can be transformed by reaction with amino acids, proteins, amino sugars, enzymes and dissolved humic matter (Jessing et al., 2009a). There are other possible degradation routes such as microbial degradation and photolysis. However, the latter one is neglected in the present study because Jessing et al. (2009a) measured the DT50 in the dark. According to Boesten et al. (1999), photochemical transformation at the soil surface before the first significant rainfall event can be relevant for many pesticides. This will possibly be as well the case for artemisinin. However, no research data has been found estimating the extent of photochemical degradation.

Similar to sorption, soil heterogeneity plays an important role on degradation. For example, degradation usually proceeds faster in the environment than in laboratory conditions due to a decrease in microbial activity with incubation time and multiple further degradation pathways operating under field conditions, resulting in more rapid degradation (Van der Werf, 1996 and Boesten, 1999). DAISY takes in the present simulation spatial differences into account such as soil temperature and soil moisture (Hansen et al., 2012). Furthermore, in the existent simulation set up and according to FOCUS (2001), degradation follows a factor that is decreasing with soil depth and neglects decomposition below 95 cm completely. That is due to the fact that photolysis is not taking place in the subsoil, it retains less organic matter, and therefore contains fewer decomposing microbial biomasses. Furthermore natural fluctuations are much less pronounced (Boesten, 1999). However, in the environment such a sharp degradation pattern for artemisinin would most likely not occur. Recent research revealed that decomposition of artemisinin might be catalysed by the reduced Fe(II), or as Jessing et. al (2009b) is claiming as well by Fe(III) and Mn(II), as it cleaves the endoperoxide bridge (Meshnick et al., 1993). Especially in the subsoil, where anaerobic conditions are likely to happen, the mentioned chemical degradation pathway with Fe(II) might prevail. Furthermore residence time of the chemical compound in the subsoil is in common higher than in the topsoil and the macropores are able to transport organic matter to the deeper soil regions where it influences decomposition. To my knowledge, no research was carried out so far in respect to degradation of artemisinin in the subsoil. Therefore it has a considerable influence of the leaching concentration of the present simulation (see chapter 4.2.3 and 4.2.4).

As a matter of fact, colloid transport plays also a substantial role in leaching of contaminants to the groundwater. Field experiments of structured soils have approved that chemical compounds associated with particulate matter, such as strongly sorbing pesticides, can move rapidly via macropores to the subsurface and from there to the groundwater or to drainage pipes (Jarvis et al., 1999). But, colloid transport have been neglected in the current study as artemisinin possesses a relatively low sorption capacity and therefore following the preferential flow and matrix leaching typically in the dissolved form. Nonetheless, as artemisnin is partitioning largely to organic matter and probably to a minor extent via surface complexation at the clay- surfaces, colloid transport with artemisinin will occur in nature as well. Jessing et al. (2009a) presented in their study on the same sandy loam soil type, geographical location and with a related *Artemisia annua* cultivar that artemisinin is able to accumulate through partitioning in SOM in the upper soil horizon. This evidence needs to be incorporated in future simulations because potential organic colloid transport (to a minor extent clay colloids), mobilized by the kinetic energy of the rain drops, increase artemisnin leaching. Furthermore, colloids might end up in macropores through physio- chemical detachment in the soil matrix (Nielsen 2010, unpublished). However, DAISY is not able to simulate the latter phenomenon and little is known to what extent the kinetic detachment on the surface might take place. Therefore it was more reasonable not to introduce more uncertainty in the simulation.

Finally, plant uptake is neglected in the current study. Jessing et al. (2012b) expect that the proportion of taking up artemisinin by plant roots or soil biota is relatively small compared to what is being sorbed, leached and degraded and the authors have no evidence to what quantitative extent such processes might occur.

4.2.2 Basic Scenario

Sandy soil

The basic scenario for the sandy soil revealed no leaching of artemisinin to the groundwater because nearly most of it got degraded in the upper soil depth (figure 8). In this way no accumulation arised below 95 cm and above the groundwater level (figure 9) although degradation is considered to be disregarded in this soil zone. However, it has to be stated that a yearly concentration between 10^{-19} and 10^{-20} g m^{-3} percolated through the subsoil (see figure 10), but as values in this concentration range are prone to numerical uncertainty, caused by limited mathematical or numerical approximations in the differential governing equations (Freitas, 2002), the leaching concentrations can be considered as zero. Therefore there is no danger of pollution according to the ecotoxicological assessment (see chapter 3.5.1).

Accumulation ascended only in the first meter soil depth each year during the releasing period between the 1st of June and the 1st of October (the content trend from 0- 100 cm depth follows the same pattern as in the depth from 0 to 250, figure 9). The erratic fluctuating artemisinin content observed was caused by complex interactions between the infiltrating water, the corresponding water flux, sorption, degradation and the artemisinin load. The main factor causing two peaks per year, were the high artemisinin loads in June and more pronounced in the second half of July, and the first two weeks in September (see table 9). As only little sorption occurred, the solute followed mostly the water flux. In this way, artemisinin accumulation occurs in the topsoil up to 29 g ha^{-1} in 2004, even though the degradation rates are considered to be non-persistent (Stephensen and Solomon, 2007).

However, as indicated in figure 10, a leaching concentration peak in June 2007 at 100 cm depth of five magnitudes higher than in other years appeared. This is caused by a very intense rain shower of about 89 mm on the same date in June 2007 (see appendix XI). When artemisnin enters the soil, either in dissolved- or particle-bounded-form, the relatively high water infiltration capacity of the sandy soil leads to a rapid incorporation into the soil profile. Furthermore, the heavy rain shower was capable to temporary cause fully saturated conditions (data not shown), and as the sandy soils possess a higher saturated hydraulic conductivity then silty or clayey soils (see table 3), water percolated relatively fast and uniform through the profile. The rapid movement increased the amount of artemisinin, by-passed the degrading upper soil profile, and reached occasionally a concentration of five magnitudes higher than in the other years at a depth of 100 cm ($4.2 * 10^{-14}$ g m^{-3}). However, as indicated in figure 10 and mentioned above, the concentration in deeper soil layers decreased to zero and caused therefore no risk for potential groundwater pollution according to the ecotoxicological assessment.

Sandy loam soil

The artemisinin balance within the soil profile of the sandy loam soil exhibited a different pattern. Again, a substantial amount between 0 and 95 cm soil depth was each year degraded (see figure 11). On the other hand, preferential flow caused by the introduced macropores, bypassed the degrading soil matrix. A considerable amount entered the macropores and was rapidly reaching a soil depth of 150 cm from where pronounced leaching, due to a low K_{FOC} and no degradation, towards the upper groundwater occurred. This incident causes artemisinin accumulation in the end of 2007 and 30 cm above the groundwater level of a total amount of 3.3 g ha^{-1} (figure 12). Although such a considerable high amount was able to reach the upper groundwater, the ecotoxicological assessment revealed no danger towards an exceedance of the threshold (see chapter 3.5.1).

Next to preferential flow, as well matrix leaching occurred in the upper 100 cm depth with substantial higher concentrations then in the sandy soil (see figure 13). Particularly again during the intensive rain event in June 2007 where a leaching concentration ten magnitudes higher than in the sandy soil was simulated. However, there are three reasons which indicate that this difference should not be that pronounced; first, the DT50 is smaller for the sandy loam soil causing faster degradation. Secondly, the up-scaling precipitation factors in each month for the sandy soil, compared to the sandy loam soil, are triggering a higher amount of infiltrating water into the soil matrix (see table 8). Lastly, the hydraulic conductivity (close to) at saturation is highest in both soil types, as the water phase is continuous, and (almost) no suction occurs due to a diminishing matric potential. Therefore during an intensive rain shower, a saturated sandy soil conducts more than the sandy loam soil which possesses with its higher clay content a higher portion of less conducting micro- and mesopores.

Despite the misleading mentioned factors, a higher amount of artemisinin is able to pass through the degrading upper 95 cm soil depth in the sandy loam soil (figure 13, preferential flow), due to the fact that artemisinin entered the soil matrix at intensive rain event pronounced through macropores. According to Abrahamsen (unpublished), the macropores in the DAISY model are typically activated when saturated soil conditions occur above an unsaturated horizon, due to a compacted small soil layer with a low conductivity such as the plow pan in this case (see table 3). If the rain intensity is higher than the flow capacity of the water pathways through the Ap-horizon (especially the intra-aggregated pathways), water will accumulate on the surface and move horizontally to the closest macropore connected to the surface (Abrahamsen, unpublished). If the water inflow exceed the flow capacity of the macropore, the hydrostatic pressure increases and the rate of water leaving the pores rises. Once the macropore are full, water will accumulate in the surface again and move towards adjacent macropores that have a better flow capacity (Abrahamsen, unpublished). Furthermore, the retaining water above the compacted plow pan will also partially end up in connected macropores. Finally, Tofteng et al., (2002) and Gjettermann et al. (2004) showed as well that macropore flow occurs still after most of the water got drained, but through connected film flow between the matrix and the macropore. Therefore, macropores are influencing artemisinin leaching to a high degree, especially during intensive rain showers. Furthermore, experimental and modelling evidence suggest that rapid preferential transport increases with increasing sorption capacity (Reichenberger et al., 2002 and McGrath et al., 2008). As the precipitation occurs on small or average amounts, weakly sorbing pesticides will follow the water flux into the slowly infiltrating soil matrix. This would be the case for artemisinin with very low organic content in the topsoil. In case of a heavy rain storm on a later date, strongly sorbing pesticides will be more susceptible for the transport by preferential flow since they are retained in the soil near the surface for a longer period of time (McGrath et al., 2008). Soil water content at the time of application and the subsequent precipitation pattern are thus important factors since they regulate whether preferential flow is triggered or not and to what extent.

Moreover, drainage pipes discharged artemisinin on distinct days into the next adjacent lake or stream (see figure 14). The values were between $1.1 * 10^{-10}$ g m^{-3} and $6.1 * 10^{-7}$ g m^{-3} where the highest drainage concentration occurred again in June 2007, released by the largest rain event. One possible way artemisinin ends up in drainage pipes is because they are directly connected with some of the macropores (Abrahamsen, unpublished). Another is through the soil matrix to the drains, due to the fact that above the drainage pipes saturated conditions arise and subsequently the potential difference will cause water flow towards the pipes. However, the drained artemisinin concentrations never exceed the ecotoxicological threshold value and therefore are of no risk (see chapter 3.5.1).

4.2.3 Scenario 1

As expected when lowering the half-live, the leaching concentration of artemisinin to the groundwater was smaller compared to the basic scenario (see figure 15). The same is true for the drained concentration which leaves the soil body and enters instantly to the next stream or lake (see appendix XII). Moreover, the artemisinin content accumulated 30 cm above the groundwater, decreased in comparison to the basic scenario from 3.3 g ha^{-1} to 1.7 g ha^{-1} (see appendix XII). Thus, the artemisnin concentrations did not exceed the threshold of the ecotoxicological assessment (see chapter 3.5.2).

However, the purpose of a sensitivity analysis is to determine which input parameters are influencing mostly the model results and should allow eliminating unimportant parameters. It should as well provide direction for further research in order to reduce parameter uncertainty and increase model accuracy (Hamby, 1994). Therefore, when referring to the artemisinin balance in the appendix XII, the artemisinin concentration ended up at 150 cm depth was mainly caused by preferential flow. There was no difference between the amount leaching via preferential flow of the basic scenario and the scenario 1 (see appendix XII, 4th figure). The same is true for the drained artemisinin concentration because there is only a small drainage concentration difference between scenario 1 and the basic scenario (see figure 14 and appendix XII 1st figure). It can be assumed that most of the artemisinin reached the drainage pipes via the macropores and therefore bypassed the degrading soil matrix. Hence, there is no interaction between the changed degradation rate and the preferential flow. It can be specified that macropores are highly influencing the model output because of the omitting degradation and sorption. Consequently, further sensitivity analysis should be carried out in order to examine the degree of influence of 'macropore-discloser' and secondly, introduction of macropores to the model have to be chosen very carefully when simulating artemisnin leaching.

4.2.4 Scenario 2

Sandy soil

Even though the artemisinin load was doubled, no leaching towards the upper groundwater occurred (see figure 16). However, as in the basic scenario there was a concentration peak in 2007, caused by the same heavy rain shower. The peak was approximately one magnitude higher than the one from the basic scenario, revealing that a higher concentration leached trough the degrading upper bulk soil. Despite that fact, all artemisinin degraded within the first 95 cm soil depth and therefore no content accumulation in the upper groundwater occurred (see appendix XIII.I) and the ecotoxicological threshold didn't exceed (chapter 3.5.3).

Although there are still uncertainties introduced in the current simulation (see chapter 4.2.1), it can be stated that these results reveal a first positive sign towards agricultural purposes cultivating *Artemisia annua* on similar soil types, comparable climatic conditions and related plant cultivars. Still, further field measurement should be done in order to verify the simulated results (i.e. soil column studies or lysimeter experiments).

Sandy loam soil

When doubling the artemisinin load on the sandy loam soil, the risk of reaching the ecotoxicological threshold in the upper groundwater increases (chapter 3.5.3). As in scenario

1, the macropores revealed a big influence and leading to a potential accumulation 30 cm above the groundwater to 2.51 * 10^{-3} mg L^{-1}, which is about one magnitude smaller than the EC10 of duckweed. However, it is of no concern because artemisinin will be highly diluted while reaching surface waters.

Moreover, the drainage concentration increased as well when doubling the artemisinin load (appendix XIII.II). Although the concentration is below the ecotoxicological threshold, it reaches directly the surface water, with only little possibility of decomposition, where it potentially causes pollution. Therefore drainage pipes directly connected to macropores are of importance.

The by-pass of the degrading upper soil matrix via preferential flow, especially connected to drainage pipes, and the relatively mobile behaviour indicates that *A.annua* should be planted carefully on soils with a high content of macropores, high-producing cultivars, and regions with intensive rain events.

However, the assumptions made in the current simulation are without considering the subsoil- degradation (see chapter 4.2.1). The accumulated content 30 cm above the groundwater will be different as artemisinin in the partially reduced soil environment will be depleted, according to the mentioned chemical degradation pathway in chapter 4.2.1. Therefore further research has to done in order to diminish this uncertainty. Furthermore, colloid transport and photochemical degradation should be incorporated when necessary.

5 Conclusion

Artemisinin possess a mobile character in the soil environment which is proven by the experimentally estimated small K_F values for the sandy and sandy loam soil. As both Ap-horizons possess larger K_F values than their corresponding subsoils, partitioning of artemisinin into organic matter is the main sorption process. Furthermore, surface complexation on clay particles occurs to a minor extent when the organic matter content decreases.

According to the simulated outcome, the leaching concentration of artemisinin in the upper groundwater never exceeded the ecotoxicological thresholds of freshwater algae *(Pseudokirchneriella sp.)* and duckweed *(Lemna minor)* in the sandy and sandy loam soil, primarily because of its fast degradation rate. Furthermore, the groundwater leads to surface water bodies which will decrease the concentration tremendously due to dilution. Notwithstanding, the sandy soil showed no leaching towards the upper groundwater at all, although no subsoil degradation was considered and the artemisinin load was doubled. Therefore, artemisinin production, with similar conditions, could be considered on the sandy soil.

On the other hand, the sandy loam soil exhibited, with a doubled artemisinin load, a concentration in the upper groundwater close to the ecotoxicological threshold, mainly due to preferential flow and intensive rain showers. Especially macropores directly connected to drainage pipes reveal a high risk as artemisinin is instantly ending up in surface water bodies. Consequently, macropores, drainage pipes, climatic conditions, and the load can be considered important. On the other hand, degradation of artemisinin is rather insignificant due the relatively low DT50-values. In this way, production of artemisinin in soils with macropores and directly connected drainage pipes, cultivation of high producing cultivars, and geographical regions with intensive rain showers during the vegetation period have to be treated with care and disclose an increased risk.

However, it is inevitably necessary to conduct further risk assessments on the fate and behaviour of artemisinin in soil before any final conclusion upon the effects of artemisinin leaching to the groundwater or to drainage pipes can be drawn. Those studies need to be adapted to climatic, genetic, managerial, and local soil conditions. Furthermore, there are factors in the current study which were omitted, such as surface runoff, subsurface degradation, photolysis, and colloid transport. Broader research needs to be conducted for these factors and, if necessary, incorporated in future simulations. Finally, it is recommended to conduct field experiments to verify the modelled outcome in order to create reliable risk assessments.

Perspectives

The cultivation of *Artemisia annua* and its subsequent production of artemisinin and related products are of high relevance to combating malaria because no existing alternatives demonstrate the same effectiveness. As this work exhibits, it is theoretically possible when considering worst case scenarios, such as a combination between preferential flow, intensive rain showers, and high yield artemisinin production, that artemisinin is able to leach with risky concentration to the groundwater and drainage pipes. Consequently, if we want be certain that artemisinin production can be carried out sustainably in rural areas close to the malaria-suffering population, further site-specific environmental risk assessments have to be conducted. This is especially true in developing countries where environmental regulations are weak. One important contribution to reach this goal would be to set up more sophisticated models, striking the balance between complexity estimated by the number of model parameters and the accuracy assessed by the simulated and measured outputs. This would further include verifying processes with field studies such as lysimeters or soil column studies. In this way, a relatively fast and economical, but solid, procedure would be achieved to make certain that environmental protective goals can be achieved.

In addition, to site-specific risk assessments and possible mitigation measures, the social impact, effectiveness, and cost-benefit analysis of such have to be included. Because the ultimate goal when carrying out such an analysis is a sustainable production of artemisinin taking into account social, environmental and economic aspects.

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Appendix

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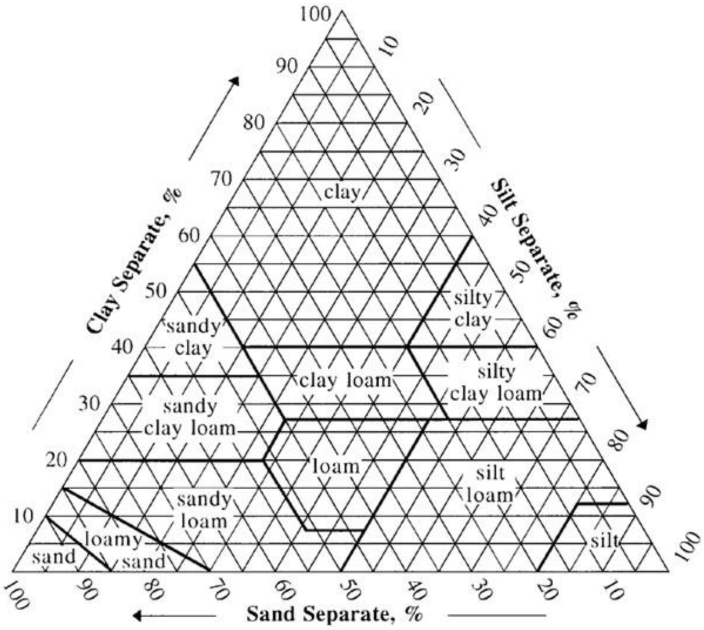
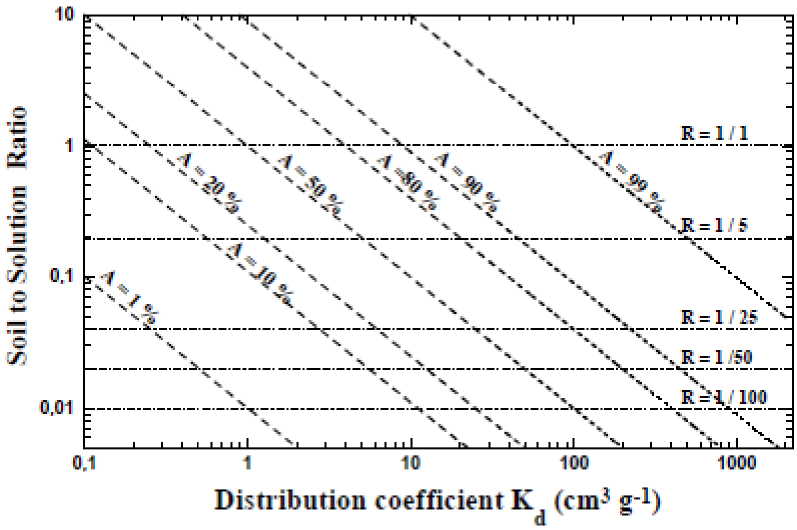
I USDA soil texture triangle



USDA soil texture triangle for the classification of the Jyndevad and Taastrup soil.

II Selection of optimal soil/solution ratio

According to OECD (2000), the selection of appropriate soil to solution ratio for sorption studies depends on Kd and the relative degree of adsorption desired. The estimated K_d according to Hermann et al. (2012) for the Taastrup soil was 6.57 L kg-1 for the topsoil, 3.29 for the subsurface and 0.92 L kg-1 for the subsoil, respectively. The adsorption percentage should be above 50% but care should be taken that artemisinin is still easily detectable in the solution. For a soil/solution ration of 1:5 a K_d of 3.29 L kg-1 and an estimated adsorbed percentage of 50% have been selected.



Relationship between soil to solution ratios and K_d at various percentages of adsorbed test substance (OECD, 2000).

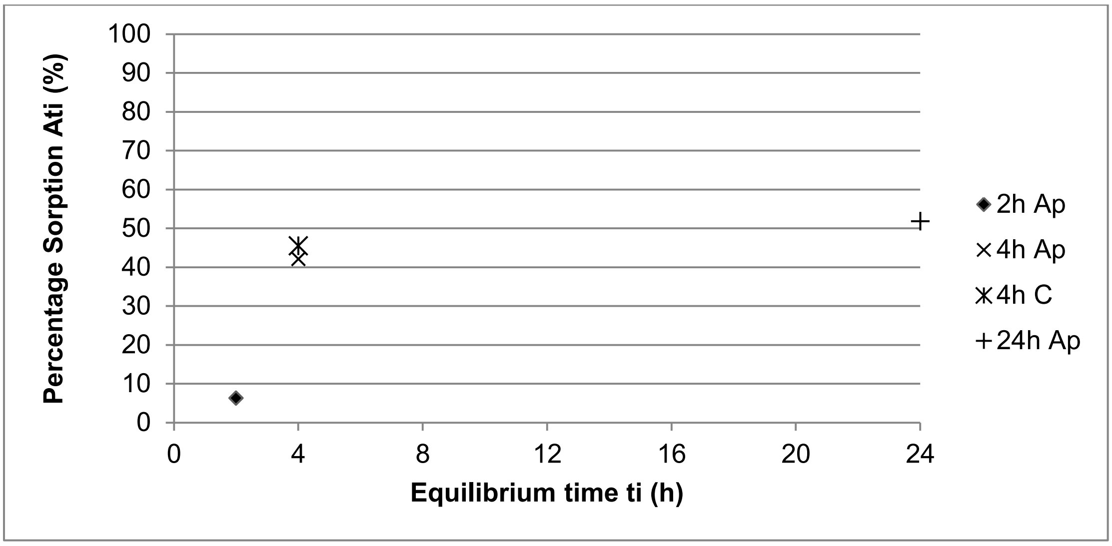
III Determination of adsorption equilibrium

The adsorption percentage has been calculated according to the equation:

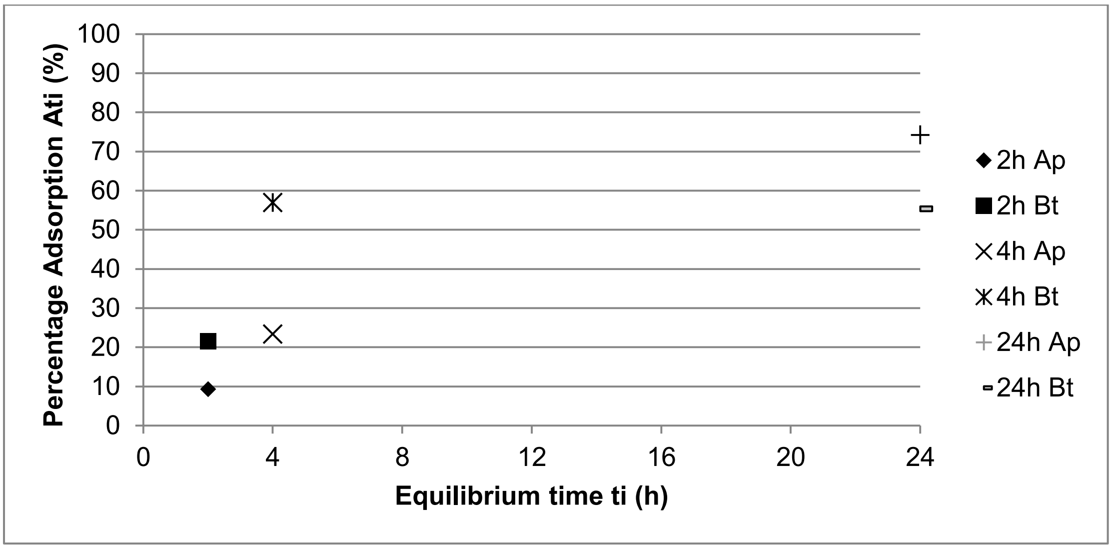
A_{ti} (%) = m_s^{ads} (t_i) * 100 / m_o

where A_{ti} is percentage of artemisinin sorbed to the soil matrix, $m_s^{ads}(t_i)$ the mass sorbed to the soil matrix after equilibrium time 'i' and m_o is the mass of artemisinin added.

Adsorption equilibrium is achieved after 4 hours. Up to 2 hours sorption is still occurring but until 24 hours the amount of sorbed artemisinin were levelled off and degradation is taking place.

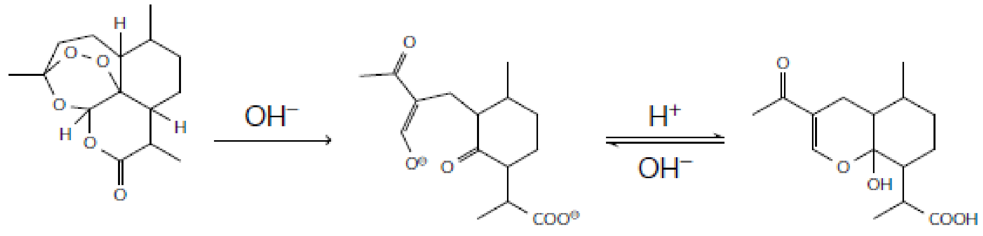


Sorption equilibrium plot for the sandy soil. For each horizon duplicates have been measured and the arithmetic mean calculated. The letters '2h', '4h' and '24h' are indicating the equilibrium time whereas the letters 'Ap' and 'C' are indicating the horizons. The samples '2h C' and '24h C' have been excluded due to deficient HPLC measurements



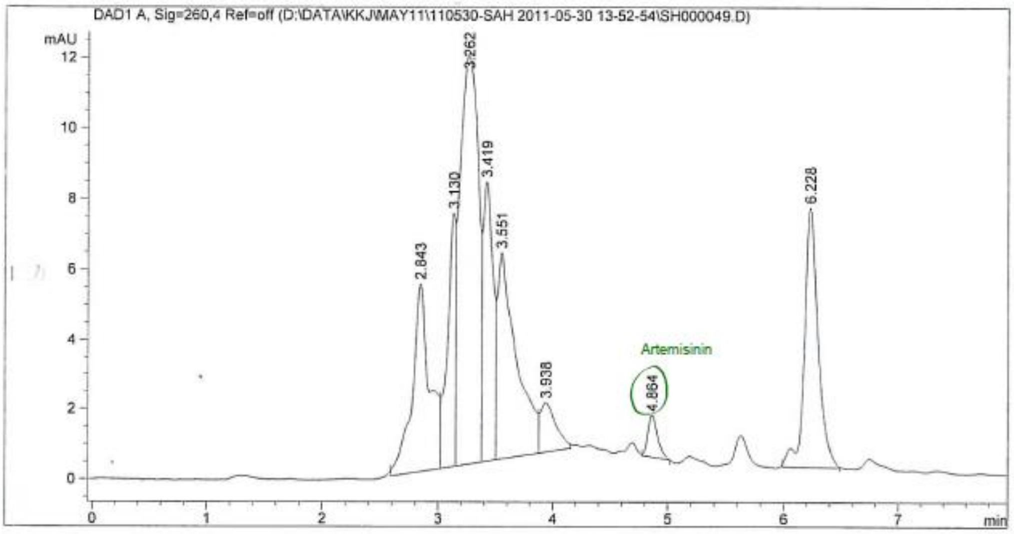
Sorption equilibrium plot for the sandy loam soil. For each horizon duplicates have been measured and the arithmetic mean calculated. The letters '2h', '4h' and '24h' are indicating the equilibrium time whereas the letters 'Ap' and 'Bt' are indicating the horizons.

IV HPLC quantification of artemisinin



Artemisinin Q292 Q260

Schematic graphs of artemisinin and its transformation to Q292, and Q260



Typical HPLC chromatogram for artemisinin determination and quantification. Retention time is ca. at 5 min.

V Determination of LOD

The table below exhibits the measured and integrated area by the HPLC in the range between 5.00 and 5.9. The corresponding artemisinin concentrations are calculated according to the standard curve in chapter VI and are in the range between 0.26 to 0.31 mg L^{-1}.

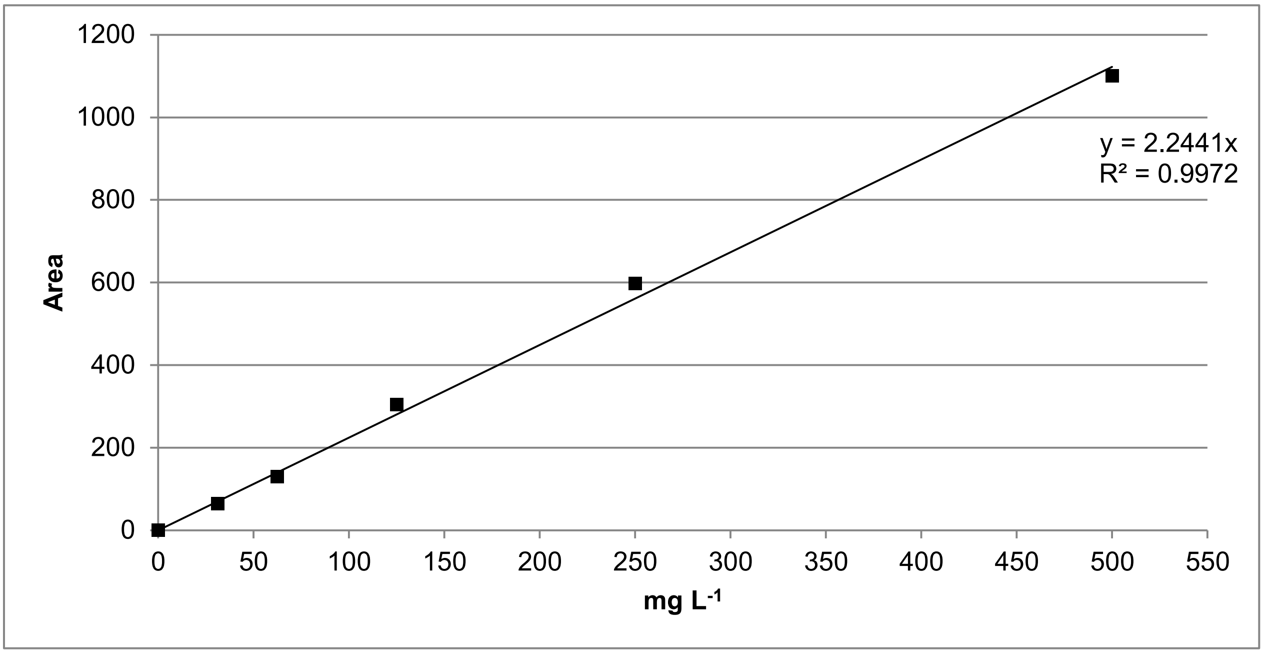
Determination of the LOD according to Boqué and Heyden (2009).

Sample Nr.	Area	Artemisinin conc. (mg L^{-1})
I	5.28	0.28
II	5.17	0.27
III	5.24	0.27
IV	5.00	0.26
V	- [a]	0.00
VI	- [a]	0.00
VII	- [a]	0.00
VIII	5.1	0.27
IX	5.9	0.31
X	- [a]	0.00

[a] not detectable because < 5.

Standard deviation: 0.14
LOD: 0.43
LOQ: 1.43

VI Recovery measurements



Standard curve for the recovery measurements, sorption equilibrium and LOD used to calculate the corresponding artemisinin concentration. The 'Area' is the integrated retention time of the HPLC measurements and the slope of the linear trend line are used to calculate the measured area of each concentration.

The table below exhibits a recovery percentage of artemisinin for each soil type between 82 and 102%. The samples for Ap- horizon of the sandy soil were not possible due to deficient HPLC measurements.

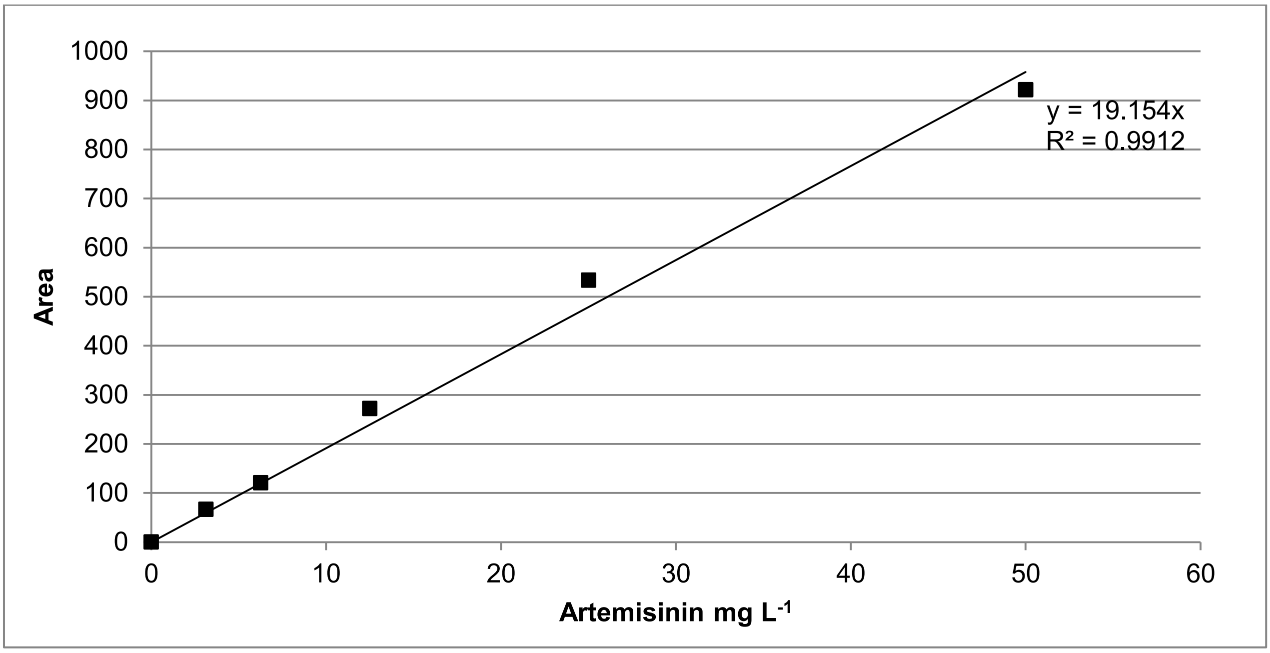
The calculated recovery percentage for each soil horizon in duplicates. The initial spiked artemisinin concentration is 31.25 mg L^{-1}, which is used as 100%.

	Area	Artemisinin conc. (mg L^{-1})	Recovery (%)
Sandy soil / Ap horizon I	-[a]	-	-
Sandy soil / Ap horizon II	-[a]	-	-
Sandy soil / C horizon I	72	31.8	102
Sandy soil / C horizon II	66	29.3	94
Sandy loam / Ap horizon I	57	25.5	82
Sandy loam / Ap horizon II	60	27	88
Sandy loam / Bt horizon I	68	30.3	97
Sandy loam / Bt horizon II	65	29.0	93

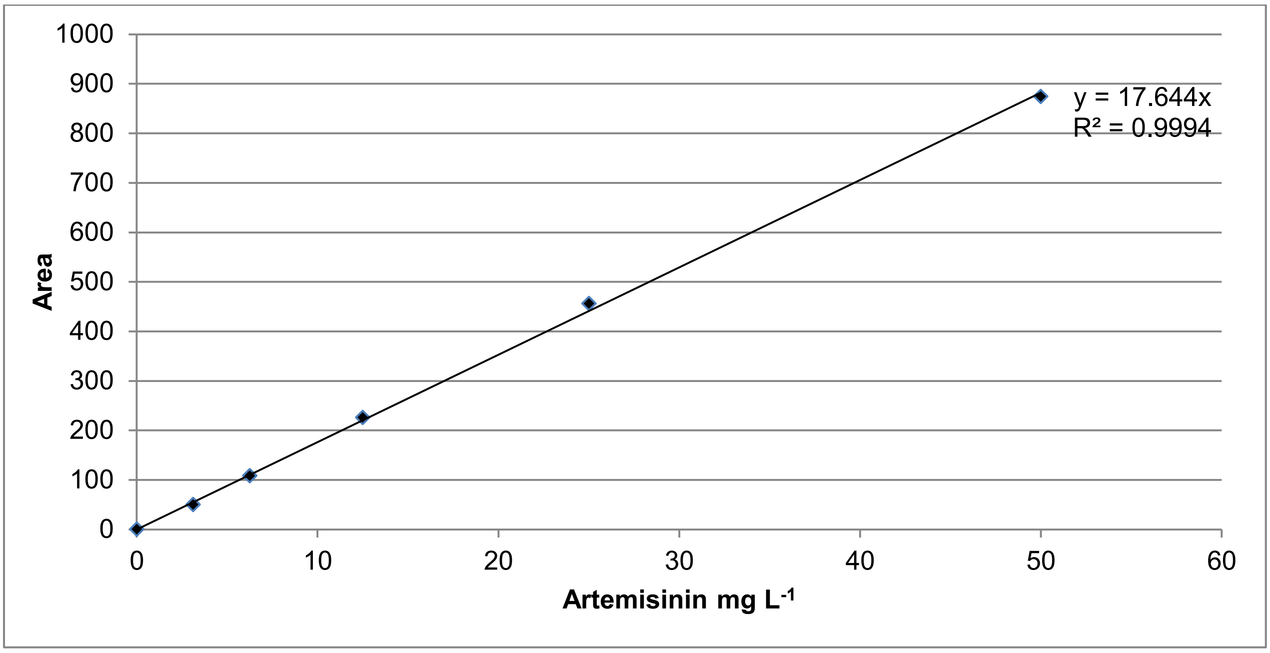
[a] No measurements possible due to deficient HPLC measurements

VII Determination and data collection of HPLC- experiment

VII.I Standard curves



Standard curve used to calculate the 50 µg mL^{-1} initial concentration, blank run and control samples. The 'Area' is the integrated retention time of the HPLC measurements and the slope of the linear trend line are used to calculate the measured area of each concentration.



Standard curves used to calculate the 40 µg mL^{-1} and 30 µg mL^{-1} initial spiked concentration. The 'Area' is the integrated retention time of the HPLC measurements and the slope of the linear trend line are used to calculate the measured area of each concentration.

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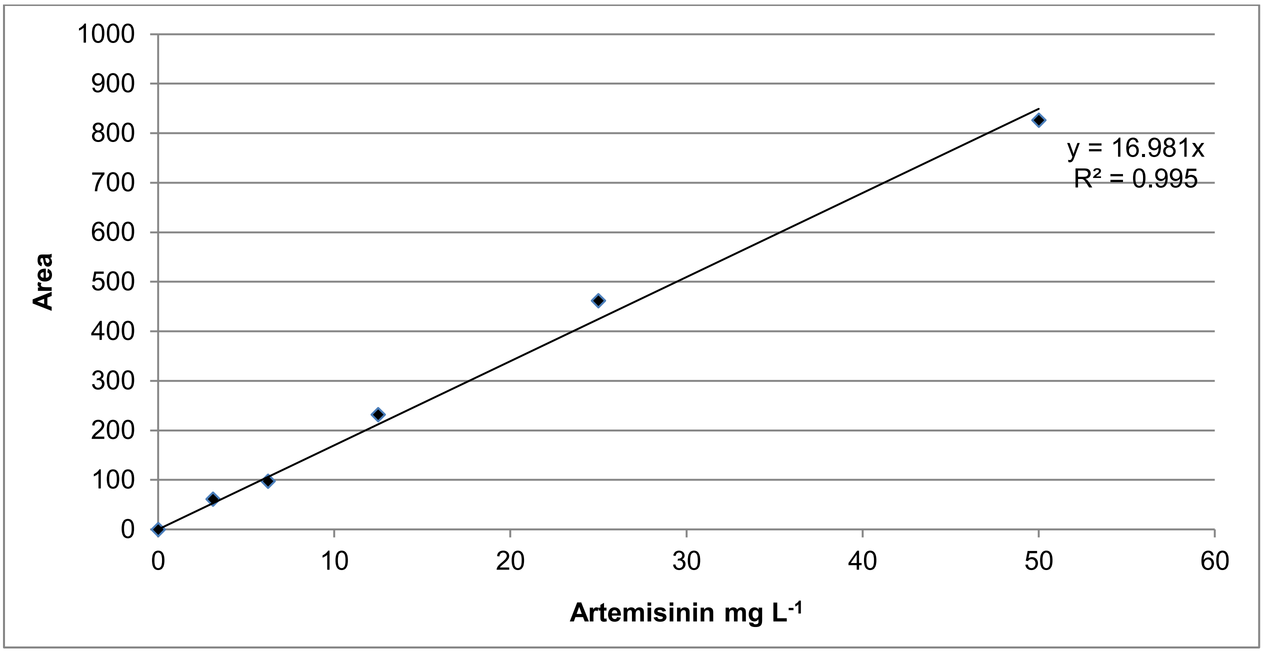


Standard curves used to calculate the 20 µg mL^{-1} and 10 µg mL^{-1} initial spiked concentration. The 'Area' is the integrated retention time of the HPLC measurements and the slope of the linear trend line are used to calculate the measured area of each concentration.

VII.II Distribution coefficient Kd

According to the OECD (2000) the distribution coefficient K_d is the ratio between the content of the substance in the solid phase and the mass concentration of the substance in the aqueous phase at equilibrium and under test condition:

K_d (L kg^{-1}) = C^{ads}_s (eq) / C^{ads}_{aq} (eq) = m^{ads}_s (eq) / m^{ads}_{aq} (eq) * Vo / m_{soil}

According to the OEDC (2000) the organic carbon normalized adsorption coefficient K_{OC} relates the distribution coefficient K_d to the content of the organic carbon:

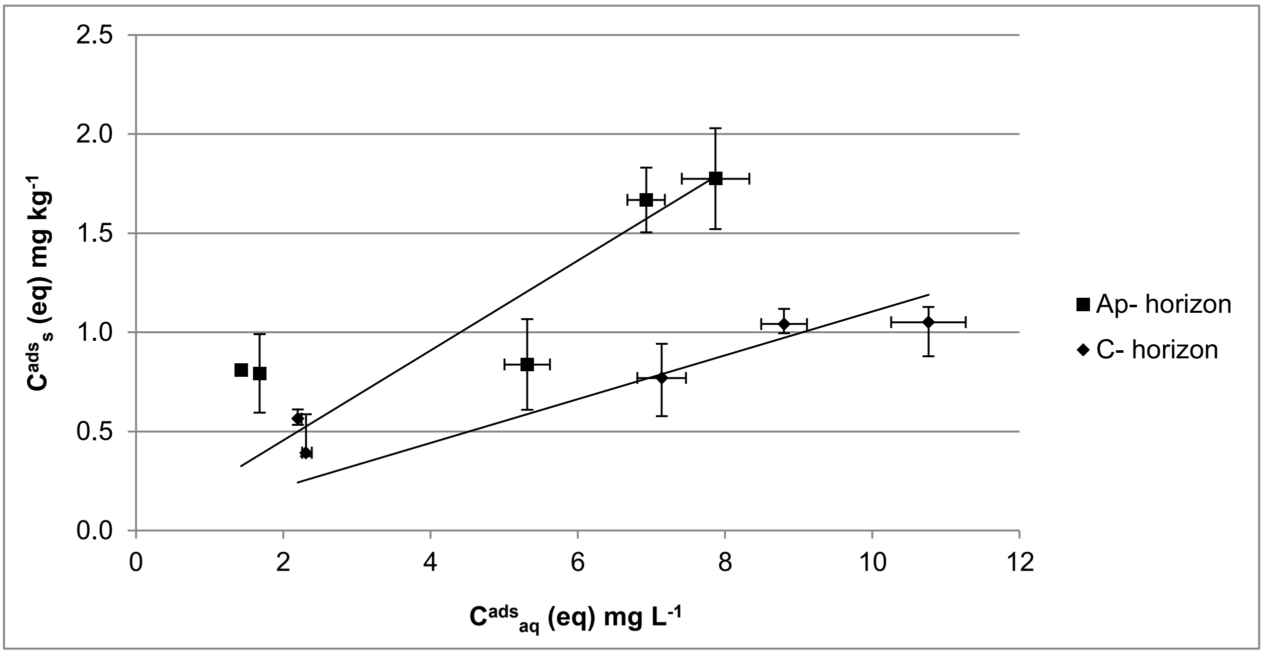
K_{oc} (L kg^{-1}) = (K_d * 100) / %oc

The K_d- values exhibit bigger values for the Ap- horizons compared to the C- and Bt- horizon. The K_{OC}- values of the Bt- horizon is the largest followed by the Ap- horizon and C- horizon of the sandy soil and the Ap- horizon of the sandy loam soil. The R^2 are low for the sandy soil and very low for the Ap- horizon of the sandy loam soil. The best fitting degree with 0.87 possess the Bt- horizon.

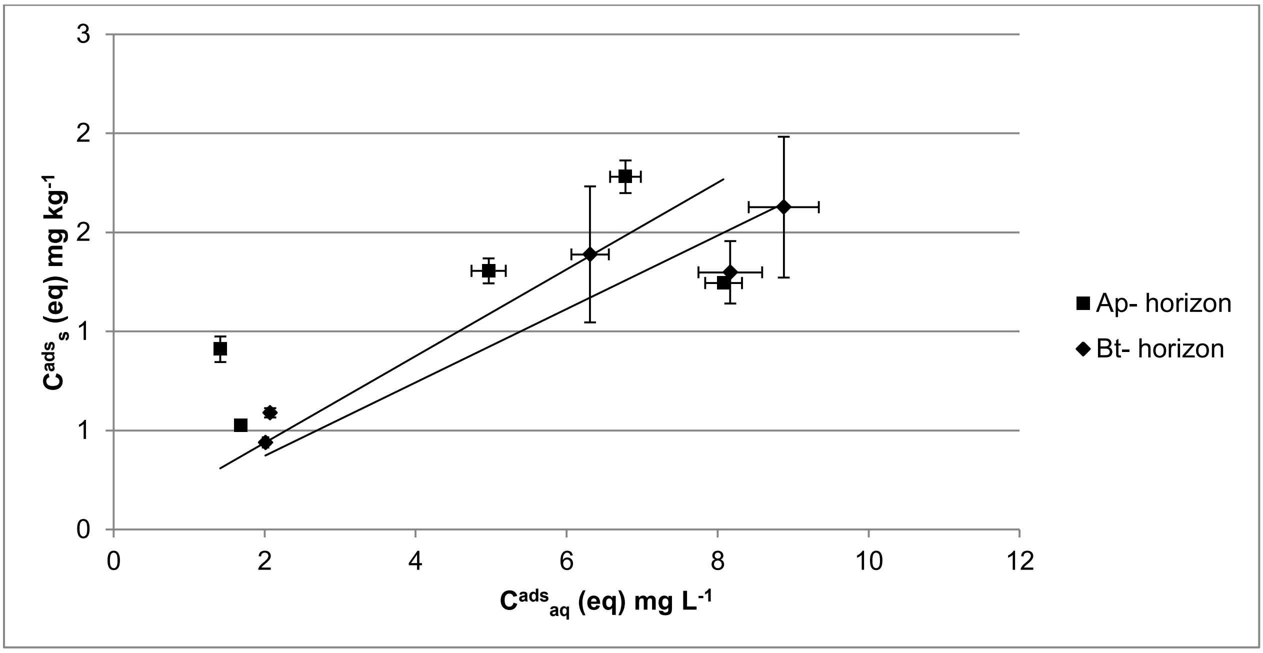
The table below shows the K_d, K_{OC} and R^2 for the sandy and sandy loam soil and their corresponding horizons. The K_d and K_{OC} is calculated according to the equation above (chapter VII.II) and R^2 according to the two figures below (chapter VII.II).

	K_d	K_{OC}	R^2
Sandy soil / Ap horizon	0.23	15.11	0.45
Sandy soil / C horizon	0.11	13.51	0.56
Sandy loam soil / Ap horizon	0.22	12.55	0.09
Sandy loam soil / Bt horizon	0.19	19.93	0.87

The Ap- horizon has a larger amount of artemisinin sorbed to the soil matrix then in the C-horizon. Moreover, the Ap- horizon possess as well a steeper slope and therefore a larger Kd- value (see table above, chapter VII.II). The error- bars are SEM of each data point which implies three samples.



Simple sorption isotherms for the sandy soil of the Ap and C horizon with its corresponding trendlines for calculating the distribution coefficient Kd. The error bars are the SEM- values for three samples per sampling point.



Simple sorption isotherms for the sandy loam soil of the Ap and C horizon with its corresponding trendlines for calculating the distribution coefficient Kd. The error bars are the SEM- values for three samples per sampling point.

VII.III Data collection

Control samples

Stock solution	Area	Art. total (µg mL^{-1})	Art. mass (µg)	Art. (µg mL^{-1})	Mean (µg mL^{-1})	Total spiked (µg)	End Art. Conc. (µg mL^{-1})
50 (10)	1334	69.63	696.25	69.63			
50 (10)	1378	71.95	719.48	71.95			
50 (10)	1337	69.78	697.77	69.78	70.45	176.13	14.09
40 (8)	496	28.08	280.80	56.16			
40 (8)	487	27.57	275.70	55.14			
40 (8)	492	27.85	278.53	55.71	55.67	139.17	11.13
30 (6)	372	21.06	210.60	42.12			
30 (6)	370	20.95	209.47	41.89			
30 (6)	359	20.32	203.24	40.65	41.55	103.88	8.31
20 (4)	117	6.89	68.90	13.78			
20 (4)							
20 (4)	117	6.89	68.90	13.78	13.78	34.45	2.76
10 (2)	61	3.59	35.92	7.18			
10 (2)	63	3.71	37.10	7.42			
10 (2)	62	3.65	36.51	7.30	7.30	18.26	1.46

14.1 µg mL^{-1} (supposed to be 10 µg mL^{-1} (50 µg mL^{-1} stock solution))

		Soil solution				**Soil matrix**				**Total**	
Soil type	**Soil (g)**	**Area**	**Art. Conc. (µg mL^{-1})**	**Art. Conc (µg mL^{-1})**	**Total mass (µg)**	**Area**	**Total (µg/2.5g Soil)**	**Soil (µg g^{-1})**	**Total mass (µg)**	**(µg)**	**MB (%)**
Sandy loam Ap I	2.50	185	9.66	7.73	96.64	61	3.21	1.28	32.06	128.69	73.07
Sandy loam Ap II	2.50	207	10.79	8.63	107.91	60	3.14	1.26	31.43	139.34	79.12
Sandy loam Ap III	2.50	188	9.84	7.87	98.36	57	2.99	1.19	29.86	128.22	72.80
Sandy loam Bt I	2.50	234	12.21	9.77	122.06	57	2.95	1.18	29.55	151.61	86.08
Sandy loam Bt II	2.50	214	11.19	8.95	111.88	117	6.12	2.45	61.19	173.07	98.27
Sandy loam Bt III	2.50	190	9.89	7.91	98.93	60	3.13	1.25	31.33	130.26	73.96
Sandy Ap I	2.50	186	9.70	7.76	96.95	61	3.18	1.27	31.79	128.75	73.10
Sandy Ap II	2.50	212	11.05	8.84	110.47	84	4.41	1.76	44.06	154.54	87.74
Sandy Ap III	2.50	168	8.77	7.02	87.71	110	5.73	2.29	57.27	144.98	82.32
Sandy C I	2.50	282	14.71	11.77	147.07	33	1.71	0.68	17.07	164.14	93.20
Sandy C I	2.50	233	12.19	9.75	121.85	53	2.77	1.11	27.72	149.58	84.93
Sandy C I	2.50	258	13.46	10.77	134.65	65	3.40	1.36	34.04	168.69	95.78

11.13 µg mL^{-1} (supposed to be 8 µg mL^{-1} (40 µg mL^{-1} stock solution))

		Soil solution				**Soil matrix**				**Total**	
Soil type	**Soil (g)**	**Area**	**Art. Conc (µg mL^{-1})**	**Art. Conc (µg mL^{-1})**	**Total mass (µg)**	**Area**	**Total (µg/2.5g Soil)**	**Soil (µg g^{-1})**	**Total mass (µg)**	**(µg)**	**MB (%)**
Sandy loam Ap I	2.50	149	8.44	6.75	84.35	87	4.93	1.97	49.25	133.61	96.00
Sandy loam Ap II	2.50	159	9.00	7.20	90.01	75	4.25	1.70	42.46	132.47	95.19
Sandy loam Ap III	2.50	141	7.98	6.39	79.82	74	4.19	1.67	41.89	121.72	87.46
Sandy loam Bt I	2.50	200	11.32	9.06	113.22	42	2.38	0.95	23.78	137.00	98.44
Sandy loam Bt II	2.50	178	10.08	8.06	100.77	61	3.45	1.38	34.53	135.30	97.22
Sandy loam Bt III	2.50	163	9.23	7.38	92.28	69	3.91	1.56	39.06	131.34	94.37

Sandy Ap I	2.50	159	9.00	7.20	90.01	57	3.23	1.29	32.27	122.28	87.86
Sandy Ap II	2.50	140	7.93	6.34	79.26	82	4.64	1.86	46.42	125.68	90.31
Sandy Ap III	2.50	160	9.06	7.25	90.58	82	4.64	1.86	46.42	137.00	98.44
Sandy C I	2.50	210	11.89	9.51	118.89	50	2.83	1.13	28.31	147.19	105.76
Sandy C I	2.50	184	10.42	8.33	104.17	42	2.38	0.95	23.78	127.94	91.93
Sandy C I	2.50	189	10.70	8.56	107.00	46	2.60	1.04	26.04	133.04	95.59

8.31 µg mL^{-1} (supposed to be 6 µg mL^{-1} (30 µg mL^{-1} stock solution))

		Soil solution				**Soil matrix**				**Total**	
Soil type	**Soil (gr.)**	**Area**	**Art. Conc. (µg mL^{-1})**	**Art. Conc (µg mL^{-1})**	**Total mass (µg)**	**Area**	**Total (µg/2.5g Soil)**	**Soil (µg g^{-1})**	**Total mass (µg)**	**(µg)**	**MB (%)**
Sandy loam Ap I	2.50	121	6.85	5.48	68.50	63	3.57	1.43	35.67	104.17	100.27
Sandy loam Ap II	2.50	106	6.00	4.80	60.01	58	3.28	1.31	32.84	92.84	89.37
Sandy loam Ap III	2.50	102	5.77	4.62	57.74	52	2.94	1.18	29.44	87.18	83.92
Sandy loam Bt I	2.50	140	7.93	6.34	79.26	95	5.38	2.15	53.78	133.04	128.07
Sandy loam Bt II	2.50	150	8.49	6.79	84.92	36	2.04	0.82	20.38	105.30	101.36
Sandy loam Bt III	2.50	128	7.25	5.80	72.46	53	3.00	1.20	30.00	102.47	98.64
Sandy Ap I	2.50	103	5.83	4.66	58.31	52	2.94	1.18	29.44	87.75	84.47
Sandy Ap II	2.50	130	7.36	5.89	73.60	45	2.55	1.02	25.48	99.07	95.37
Sandy Ap III	2.50	119	6.74	5.39	67.37	14	0.79	0.32	7.93	75.29	72.48
Sandy C I	2.50	141	7.98	6.39	79.82	52	2.94	1.18	29.44	109.26	105.18
Sandy C I	2.50	164	9.28	7.43	92.84	18	1.02	0.41	10.19	103.03	99.18
Sandy C I	2.50	168	9.51	7.61	95.11	32	1.81	0.72	18.12	113.22	108.99

2.76 µg mL^{-1} (supposed to be 4 µg mL^{-1} (20 µg mL^{-1} stock solution))

		Soil solution				**Soil matrix**				**Total**	
Soil type	**Soil (gr.)**	**Area**	**Art. Conc. (µg mL^{-1})**	**Art. Conc (µg mL^{-1})**	**Total mass (µg)**	**Area**	**Total (µg/2.5g Soil)**	**Soil (µg g^{-1})**	**Total mass (µg)**	**(µg)**	**MB (%)**
Sandy loam Ap I	2.50	29	1.71	1.37	17.08	44	2.59	1.04	25.91	42.99	124.79

Sandy loam Ap II	2.50	31	1.83	1.46	18.26	33	1.94	0.78	19.43	37.69	109.40
Sandy loam Ap III	2.50	30	1.77	1.41	17.67	39	2.30	0.92	22.97	40.63	117.95
Sandy loam Bt I	2.50	44	2.59	2.07	25.91	27	1.59	0.64	15.90	41.81	121.37
Sandy loam Bt II	2.50	44	2.59	2.07	25.91	23	1.35	0.54	13.54	39.46	114.53
Sandy loam Bt III	2.50	44	2.59	2.07	25.91	25	1.47	0.59	14.72	40.63	117.95
Sandy Ap I	2.50	28	1.65	1.32	16.49	33	1.94	0.78	19.43	35.92	104.27
Sandy Ap II	2.50	34	2.00	1.60	20.02	36	2.12	0.85	21.20	41.22	119.66
Sandy Ap III	2.50	29	1.71	1.37	17.08	34	2.00	0.80	20.02	37.10	107.69
Sandy C I	2.50	45	2.65	2.12	26.50	25	1.47	0.59	14.72	41.22	119.66
Sandy C I	2.50	49	2.89	2.31	28.86	26	1.53	0.61	15.31	44.17	128.21
Sandy C I	2.50	46	2.71	2.17	27.09	21	1.24	0.49	12.37	39.46	114.53

1.46 μg mL^{-1} (supposed to be 2 μg mL^{-1} (10 μg mL^{-1} stock solution))

		Soil solution				**Soil matrix**				**Total**	
Soil type	**Soil (gr.)**	**Area**	**Art. Conc. (μg mL^{-1})**	**Art. Conc (μg mL^{-1})**	**Total mass (μg)**	**Area**	**Total (μg/2.5g Soil)**	**Soil (μg g^{-1})**	**Total mass (μg)**	**(μg)**	**MB (%)**
Sandy loam Ap I	2.50	34	2.00	1.60	20.02	24	1.41	0.57	14.13	34.16	187.10
Sandy loam Ap II	2.50	36	2.12	1.70	21.20	21	1.24	0.49	12.37	33.57	183.87
Sandy loam Ap III	2.50	37	2.18	1.74	21.79	22	1.30	0.52	12.96	34.74	190.32
Sandy loam Bt I	2.50	43	2.53	2.03	25.32	18	1.06	0.42	10.60	35.92	196.77
Sandy loam Bt II	2.50	44	2.59	2.07	25.91	19	1.12	0.45	11.19	37.10	203.23
Sandy loam Bt III	2.50	41	2.41	1.93	24.14	19	1.12	0.45	11.19	35.33	193.55
Sandy Ap I	2.50	33	1.94	1.55	19.43	30	1.77	0.71	17.67	37.10	203.23
Sandy Ap II	2.50	37	2.18	1.74	21.79	19	1.12	0.45	11.19	32.98	180.65
Sandy Ap III	2.50	37	2.18	1.74	21.79	52	3.06	1.22	30.62	52.41	287.10
Sandy C I	2.50	53	3.12	2.50	31.21	15	0.88	0.35	8.83	40.04	219.35
Sandy C I	2.50	47	2.77	2.21	27.68	18	1.06	0.42	10.60	38.28	209.68
Sandy C I	2.50	47	2.77	2.21	27.68	17	1.00	0.40	10.01	37.69	206.45

Recalculation for sandy loam soil / Ap- horizon

	Soil solution								**Soil matrix**							
	Non-linear for K_d				**Log for K_F**				**Non-linear for K_d**				**Log for K_F**			
Initial conc. mg/L	*eq Cw mg/L*	*Mean eq Cw mg/L*	*STDEV*	*CV %*	*log Cw mg/L*	*Mean log mg/L*	*STDEV*	*CV %*	*eq Cs mg/kg*	*Mean eq Cs mg/kg*	*STDEV*	*CV %*	*Log Cs mg/kg*	*Mean log mg/kg*	*STDEV*	*CV %*
14.4	7.73					0.89					1.28					0.11
	8.63					0.94					1.26					0.10
	7.87	8.08	0.49	0.24	6.02	0.90	0.91	0.03	0.01	2.84	1.19	1.24	0.05	0.02	3.63	0.08
11.1	6.75					0.83					1.97					0.29
	7.20					0.86					1.70					0.23
	6.39	6.78	0.41	0.20	6.03	0.81	0.83	0.03	0.01	3.14	1.67	1.78	0.16	0.08	9.21	0.22
8.3	5.48					0.74					1.43					0.15
	4.80					0.68					1.31					0.12
	4.62	4.97	0.45	0.23	9.13	0.66	0.69	0.04	0.02	5.60	1.18	1.31	0.12	0.06	9.54	0.07
2.5	1.37					0.14					1.04					0.01
	1.46					0.16					0.78					-0.11
	1.41	1.41	0.05	0.02	3.33	0.15	0.15	0.01	0.01	9.65	0.92	0.91	0.13	0.06	14.18	-0.04
1.1	1.60					0.20					0.57					-0.25
	1.70					0.23					0.49					-0.31
	1.74	1.68	0.07	0.04	4.28	0.24	0.23	0.02	0.01	8.32	0.52	0.53	0.04	0.02	6.84	-0.29

Recalculation for Loamy sand soil / Bt- horizon

	Soil solution								**Soil matrix**							
	Non-linear for K_d				**Log for K_F**				**Non-linear for K_d**				**Log for K_F**			
Initial conc. mg/L	*eq Cw mg/L*	*Mean eq Cw mg/L*	*STDEV*	*CV %*	*log Cw mg/L*	*Mean log mg/L*	*STDEV*	*CV %*	*eq Cs mg/kg*	*Mean eq Cs mg/kg*	*STDEV*	*CV %*	*Log Cs mg/kg*	*Mean log mg/kg*	*STDEV*	*CV %*
14.4	9.77				0.99				1.18				0.07			
	8.95				0.95				2.45				0.39			
	7.91	8.88	0.93	10.45	0.90	0.95	0.05	4.84	1.25	1.63	0.71	43.68	0.10	0.19	0.18	94.24
11.1	9.06				0.96				0.95				-0.02			
	8.06				0.91				1.38				0.14			
	7.38	8.17	0.84	10.32	0.87	0.91	0.04	4.89	1.56	1.30	0.31	24.19	0.19	0.10	0.11	107.89
8.3	6.34				0.80				2.15				0.33			
	6.79				0.83				0.82				-0.09			
	5.80	6.31	0.50	7.91	0.76	0.80	0.03	4.32	1.20	1.39	0.69	49.51	0.08	0.11	0.21	197.14
2.5	2.07				0.32				0.64				-0.20			
	2.07				0.32				0.54				-0.27			
	2.07	2.07	0.00	0.00	0.32	0.32	0.00	0.00	0.59	0.59	0.05	8.01	-0.23	-0.23	0.03	-15.09
1.1	2.03				0.31				0.42				-0.37			
	2.07				0.32				0.45				-0.35			
	1.93	2.01	0.07	3.58	0.29	0.31	0.01	2.27	0.45	0.44	0.01	3.10	-0.35	-0.36	0.01	-3.81

Recalculation for Sandy soil / Ap- horizon

	Soil solution								**Soil matrix**							
	Non-linear for K_d				**Log for K_F**				**Non-linear for K_d**				**Log for K_F**			
Initial conc. mg/L	*eq Cw mg/L*	*Mean eq Cw mg/L*	*STDEV*	*CV %*	*log Cw mg/L*	*Mean log mg/L*	*STDEV*	*CV %*	*eq Cs mg/kg*	*Mean eq Cs mg/kg*	*STDEV*	*CV %*	*Log Cs mg/kg*	*Mean log mg/kg*	*STDEV*	*CV %*
14.4	7.76									1.27					0.10	
	8.84									1.76					0.25	
	7.02	7.87	0.92	0.46	11.64	0.89	0.05	0.03	5.62	2.29	1.77	0.51	0.25	28.73	0.36	0.24
11.1	7.20									1.29					0.11	
	6.34									1.86					0.27	
	7.25	6.93	0.51	0.26	7.37	0.84	0.03	0.02	3.90	1.86	1.67	0.33	0.16	19.59	0.27	0.22
8.3	4.66									1.18					0.07	
	5.89									1.02					0.01	
	5.39	5.31	0.61	0.31	11.57	0.72	0.05	0.03	7.05	0.32	0.84	0.46	0.23	54.66	-0.50	-0.14
2.5	1.32									0.78					-0.11	
	1.60									0.85					-0.07	
	1.37	1.43	0.15	0.08	10.60	0.15	0.04	0.02	29.28	0.80	0.81	0.04	0.02	4.47	-0.10	-0.09
1.1	1.55									0.71					-0.15	
	1.74									0.45					-0.35	
	1.74	1.68	0.11	0.05	6.47	0.22	0.03	0.01	12.76	1.22	0.79	0.40	0.20	49.93	0.09	-0.14

Recalculation for Sandy soil / Bt- horizon

	Soil solution								**Soil matrix**							
	Non-linear for K_d				**Log K_F**				**Non-linear for K_d**				**Log K_F**			
Initial conc. mg/L	*eq Cw mg/L*	*Mean eq Cw mg/L*	*STDEV*	*CV %*	*log Cw mg/L*	*Mean log mg/L*	*STDEV*	*CV %*	*eq Cs mg/kg*	*Mean eq Cs mg/kg*	*STDEV*	*CV %*	*Log Cs mg/kg*	*Mean log mg/kg*	*STDEV*	*CV %*
14.4	11.77				1.07				0.68				-0.17			
	9.75				0.99				1.11				0.04			
	10.77	10.76	1.01	9.37	1.03	1.03	0.04	3.97	1.36	1.05	0.34	32.62	0.13	0.00	0.15	#####
11.1	9.51				0.98				1.13				0.05			
	8.33				0.92				0.95				-0.02			
	8.56	8.80	0.62	7.10	0.93	0.94	0.03	3.21	1.04	1.04	0.09	8.70	0.02	0.02	0.04	229.38
8.3	6.39				0.81				1.18				0.07			
	7.43				0.87				0.41				-0.39			
	7.61	7.14	0.66	9.24	0.88	0.85	0.01	0.87	0.72	0.77	0.39	50.26	-0.14	-0.15	0.23	#####
2.5	2.12				0.33				0.59				-0.23			
	2.31				0.36				0.61				-0.21			
	2.17	2.20	0.10	4.46	0.34	0.34	0.02	5.62	0.49	0.57	0.06	10.99	-0.31	-0.25	0.05	-19.70
1.1	2.50				0.40				0.35				-0.45			
	2.21				0.35				0.42				-0.37			
	2.21	2.31	0.16	7.07	0.35	0.36	0.03	8.31	0.40	0.39	0.04	9.21	-0.40	-0.41	0.04	-9.98

VIII Mobility of substances

Table 1: Mobility of substances in the soil according to McCall et al. 1980.

Mobility in soil	K_{OC} L kg^{-1}
Very large	0-50
Large	50-150
Medium	150-500
Low	500- 2000
Very small	2000 - 5000
Immobile	> 5000

IX Evaluation of RMSE

RMSE were used to compare both K_F and K_d-values. The assessment for each horizon is stated in the tables below.

$$\mathbf{RMSE} = \left(\sum_{i=1}^{n} \frac{(Pi - Oi)^2}{n}\right)^{0.5}$$

where P_i is the predicted value, O_i is the observed value, and n the sampling numbers.

Sandy loam soil Ap- horizon

		KF			**Kd**		
Adapted C^{ads}_{aq} (eq) mg/L	**Normal C^{ads}_{s} (eq) mg/L**	**C^{ads}_{s} (eq) mg/L**	**Normal C^{ads}_{s} (eq) – KF C^{ads}_{s} (eq)**	x^2	**C^{ads}_{s} (eq) mg/L**	**Normal C^{ads}_{s} (eq) – Kd C^{ads}_{s} (eq)**	x^2
10		1.70					
8.077686123	1.24	1.54	0.29	0.08579	1.767397724	0.52	0.273
6.778381643	1.78	1.42	-0.36	0.13178	1.483109903	-0.30	0.089
4.96678744	1.31	1.23	-0.08	0.00602	1.086733092	-0.22	0.048
3		0.97					
1.413344326	0.91	0.69	-0.22	0.04981	0.309239739	-0.60	0.361
1.680309365	0.53	0.74	0.22	0.04765	0.367651689	-0.16	0.025
1		0.59					
		Arithmetic mean		0.06421	Arithmetic mean		0.159
		Arithmetic mean / 5		0.01284	Arithmetic mean / 5		0.032
		RMS for Freundlich		**0.113322003**	**RMS for Kd**		**0.178466931**

Sandy loam soil Bt- horizon

		KF			**Kd**		
Adapted C^{ads}_{aq} (eq) mg/L	**Normal C^{ads}_{s} (eq) mg/L**	**C^{ads}_{s} (eq) mg/L**	**Normal C^{ads}_{s} (eq) – KF C^{ads}_{s} (eq)**	x^2	**C^{ads}_{s} (eq) mg/L**	**Normal C^{ads}_{s} (eq) – Kd C^{ads}_{s} (eq)**	x^2
10		1.64					
8.876864711	1.63	1.50	0.12	0.0155	1.65	0.02	0.00034
8.167270531	1.30	1.41	-0.11	0.0132	1.51	0.22	0.04670
6.310386473	1.39	1.17	0.22	0.0485	1.17	-0.22	0.04774
4		0.83					
2.072905011	0.59	0.51	0.08	0.0058	0.38	-0.21	0.04231
2.010089708	0.44	0.50	-0.06	0.0039	0.37	-0.07	0.00453
1		0.30					
		Arithmetic mean		0.01738	Arithmetic mean		0.028
		Arithmetic mean / 5		0.00348	Arithmetic mean / 5		0.006
		RMS for Freundlich		**0.058961708**	**RMS for Kd**		**0.075265867**

Sandy soil Ap-horizon

		KF			**Kd**		
Adapted C^{ads}_{aq} (eq) mg/L	**Normal C^{ads}_{s} (eq) mg/L**	**C^{ads}_{s} (eq) mg/L**	**Normal C^{ads}_{s} (eq) – KF C^{ads}_{s} (eq)**	x^2	**C^{ads}_{s} (eq) mg/L**	**Normal C^{ads}_{s} (eq) – Kd C^{ads}_{s} (eq)**	x^2
10		1.55					
7.870244683	1.77	1.41	0.36	0.1323	1.79	-0.01	0.00012
6.929347826	1.67	1.34	0.33	0.1074	1.57	0.10	0.00916
5.314009662	0.84	1.20	-0.37	0.1340	1.21	-0.37	0.13541
3		0.96					
1.429048152	0.81	0.71	0.10	0.0101	0.32	0.48	0.23417
1.680309365	0.79	0.76	0.04	0.0014	0.38	0.41	0.16920
1		0.61					
		Arithmetic mean		0.07703	Arithmetic mean		0.110
		Arithmetic mean / 5		0.01541	Arithmetic mean / 5		0.022
		RMS for Freundlich		**0.124120404**	**RMS for linearized**		**0.148060612**

Sandy soil C-horizon

		K_F			**K_d**		
Adapted C^{ads}_{aq} (eq) mg/L	**Normal C^{ads}_{s} (eq) mg/L**	**C^{ads}_{s} (eq) mg/L**	**Normal C^{ads}_{s} (eq) – KF C^{ads}_{s} (eq)**	x^2	**C^{ads}_{s} (eq) mg/L**	**Normal C^{ads}_{s} (eq) – Kd C^{ads}_{s} (eq)**	x^2
12		1.06					
10.76189482	1.05096484	1.01	0.04	0.0020	1.19	-0.14	0.01911
8.801328502	1.04142156	0.91	0.13	0.0169	0.97	0.07	0.00474
7.140700483	0.769846628	0.82	-0.05	0.0027	0.79	-0.02	0.00037
6		0.75					
4		0.62					
2.198535618	0.565004438	0.46	0.11	0.0111	0.24	0.32	0.10373
2.308462399	0.392317374	0.47	-0.08	0.0062	0.26	0.14	0.01883
1		0.3116					
		Arithmetic mean		0.00778	Arithmetic mean		0.029
		Arithmetic mean / 5		0.00156	Arithmetic mean / 5		0.006
		RMS for Freundlich		**0.039455842**	**RMS for linearized**		**0.07662318**

X Model parameterisation

X.I Sorption calculations

For the basic simulation a K_{FOC} of 32.92 and 1/n of 0.60 for the sandy loam soil were used (see table below chapter X.I.). For the sandy soil a K_{FOC} of 41.94 and a 1/n of 0.45.

The table exhibits the calculations of the K_F and K_d values and their corresponding parameters. The 'Average used' are the used values in the simulation.

Soil	K_F	Humus % (or SOM)	K_{humus}	OC %	K_{FOC}	1/n	K_d	K_{OC}
Sandy loam Ap	0.585	**3**	19.52	**1.74**	33.57	0.462	0.22	**12.54**
Sandy loam Bt	0.300	**1.6**	18.76	**0.93**	32.27	0.74	0.19	**19.93**
Average used	0.443				**32.92**	**0.60**		
Sandy Ap	0.612	**2.3**	26.62	**1.34**	45.79	0.41	0.23	**16.98**
Old sandy C	0.310	**1.4**	22.14	**0.81**	**38.09**	0.49	0.11	**13.51**
Average used					**41.94**	**0.45**		

X.II Artemisinin load

The highest artemisinin load is according to Jessing et al. (2012a) between the 1th of July until the 15th of July. The lowest between the 15th of September until the 1th of October.

The table shows the artemisinin load of the present study for the basic simulation. It is assumed that on the 1th of June the plant begins to release artemisinin until the 1th of October. According to Jessing et al. (2012a), artemisinin was measured within the upper soil depth of 5 cm every two week and projected to g ha^{-1} (column 'Soil content'). The column 'Difference soil content' is the artemisinin content freshly accumulated in two weeks in the upper 5 cm soil depth. The column 'Artemisinin load' is the artemisinin content according to the latter column and divided by 14. In this way the flux density of artemisinin (load) ending up in the soil is calculated.

Dates	Age of plants (weeks)	Soil content (g ha^{-1})	Difference soil content (g ha^{-1})	Artemisinin load (g ha^{-1} day^{-1})
1th June	11	33.02		
15th June	13	58.72	25.70	1.8355
1th July	15	80.70	21.98	1.5699
15th July	17	123.11	42.41	3.0293
1th August	19	135.35	12.25	0.8748
15th August	21	145.97	10.62	0.7586
1th September	24	178.15	32.18	2.2985
15th September	26	185.85	7.70	0.5500
1th October	28	192.91	7.05	0.5037

X.III Important chemical properties of atrazine

The pesticide atrazine reveal similar chemical properties as artemisinin which are stated in the table below. According to (Solomon, 1996), atrazine is considered to be ecologically important in the aquatic environment at exposures of 50 µg L^{-1} or greater.

The table exhibits all important chemical properties of atrazine according to Food and Environment Protection Act (1992).

Scientific information	Value
Water solubility	33 mg L^{-1}
Henry's law constant KH	6.1 atm m^3 mol^{-1}
Log Kow	2.7
Log Koc	2.23
DT 50 ranges in sandy loam soil	From 6 to 14 days[a]

[a] organic matter content 1% and pH range from 5 to 7

X.IV Artemisinin load for scenario 2

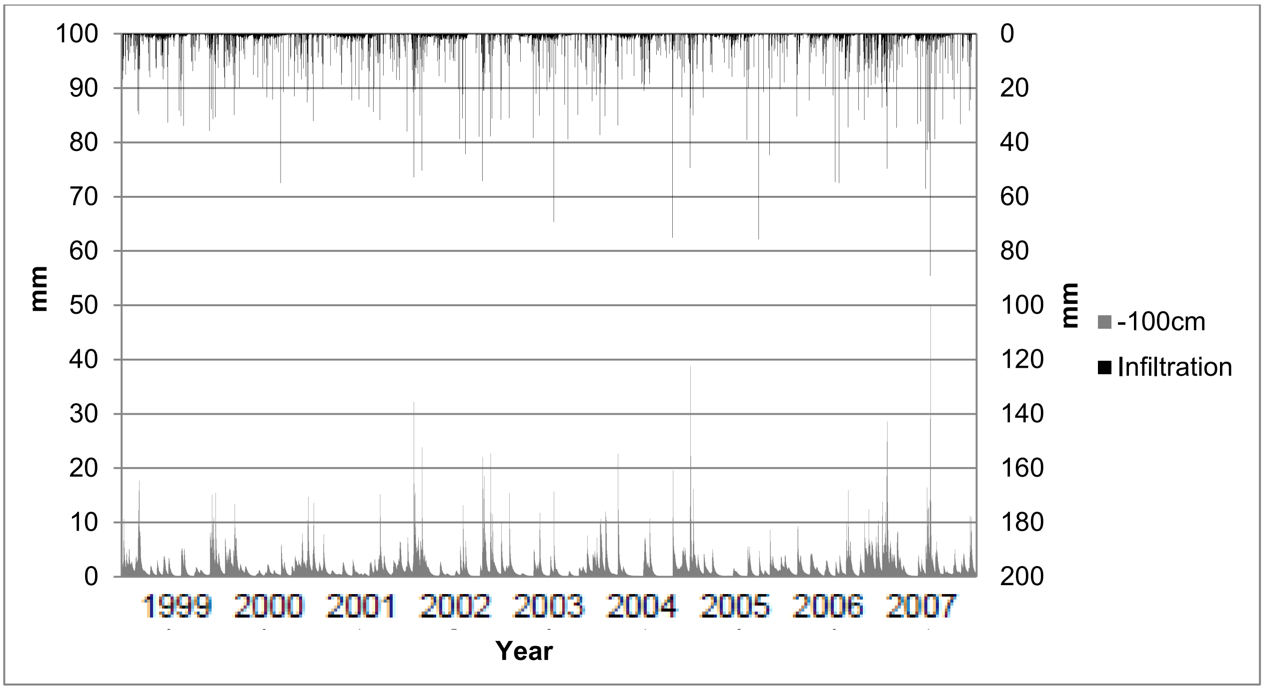
In comparison to the basic scenario, the artemisinin load was doubled and showed in the table below.

The table exhibits the artemisinin load for scenario 2. It is calculated in the same way as in chapter X.IV.

Dates	Age of plants (weeks)	Artemisinin load (g ha^{-1} day^{-1})
1th June	11	
15th June	13	3.671
1th July	15	3.1398
15th July	17	6.0586
1th August	19	1.7496
15th August	21	1.5172
1th September	24	4.597
15th September	26	1.1
1th October	28	1.0074

XI Basic scenario extra figures

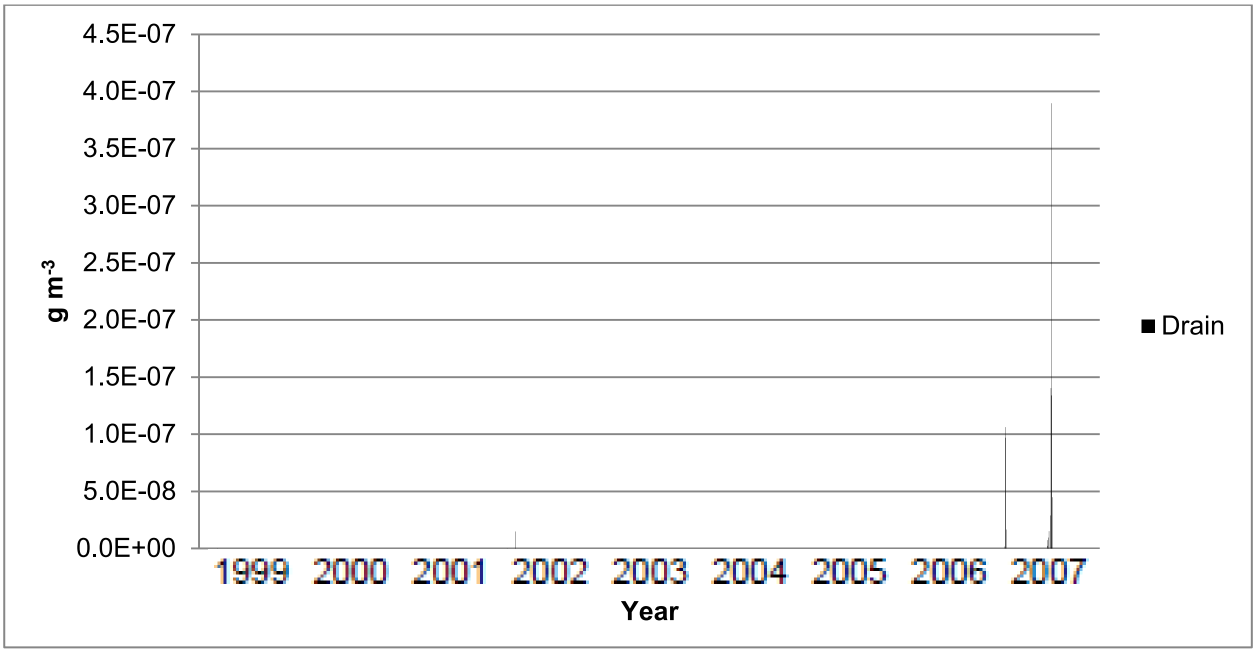
The infiltrating water over the whole simulation period reveals several heavy rain showers and especially one in June 2007 with an amount of 89 mm (figure 10). The percolation pattern at 100 cm exhibits as well several peaks with the highest (50 mm) on the same day in June 2007.



Percolation trend (primary vertical x-axis) from 0 to 100 cm depth and infiltration trend (secondory vertical x-axis) in the sandy soil for the basic scnerio over the whole simulation period (1999- 2007).

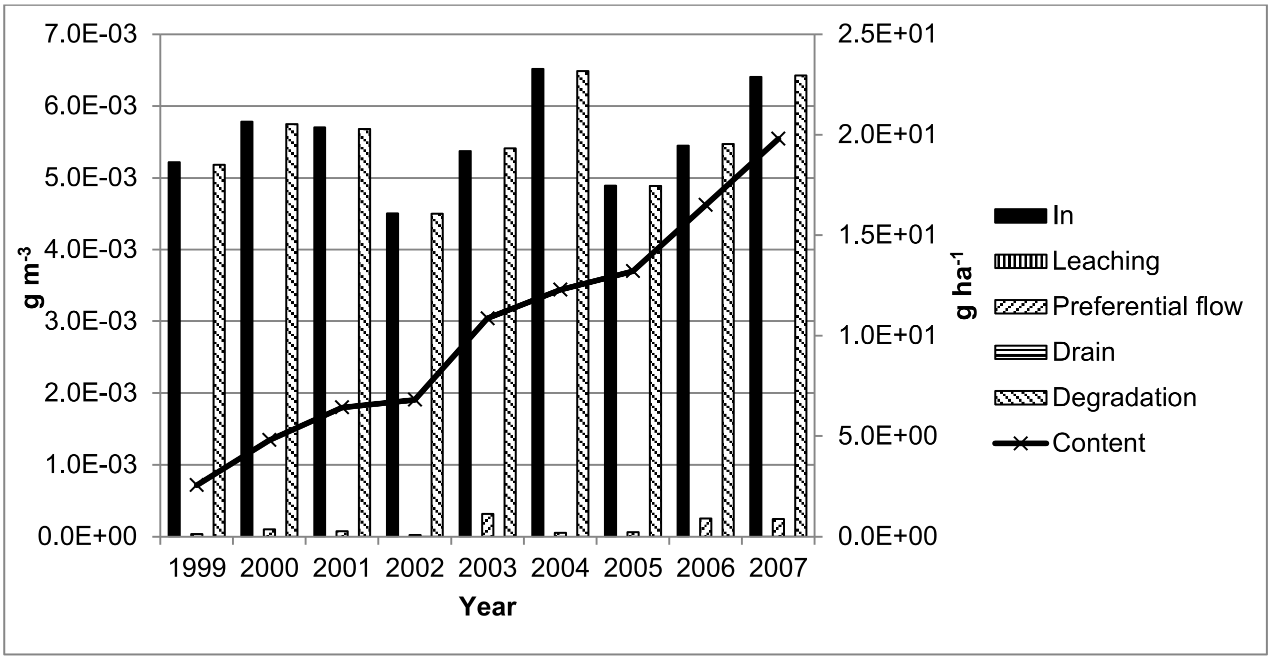
XII Scenario 1 extra figures

Drained artemisinin concentration is presented in the figure below and reveals a fluctuating pattern. The drained concentration ranges from 6.9 * 10^{-11} g m^{-3} to 3.9 * 10^{-7} g m^{-3} both in 2007.



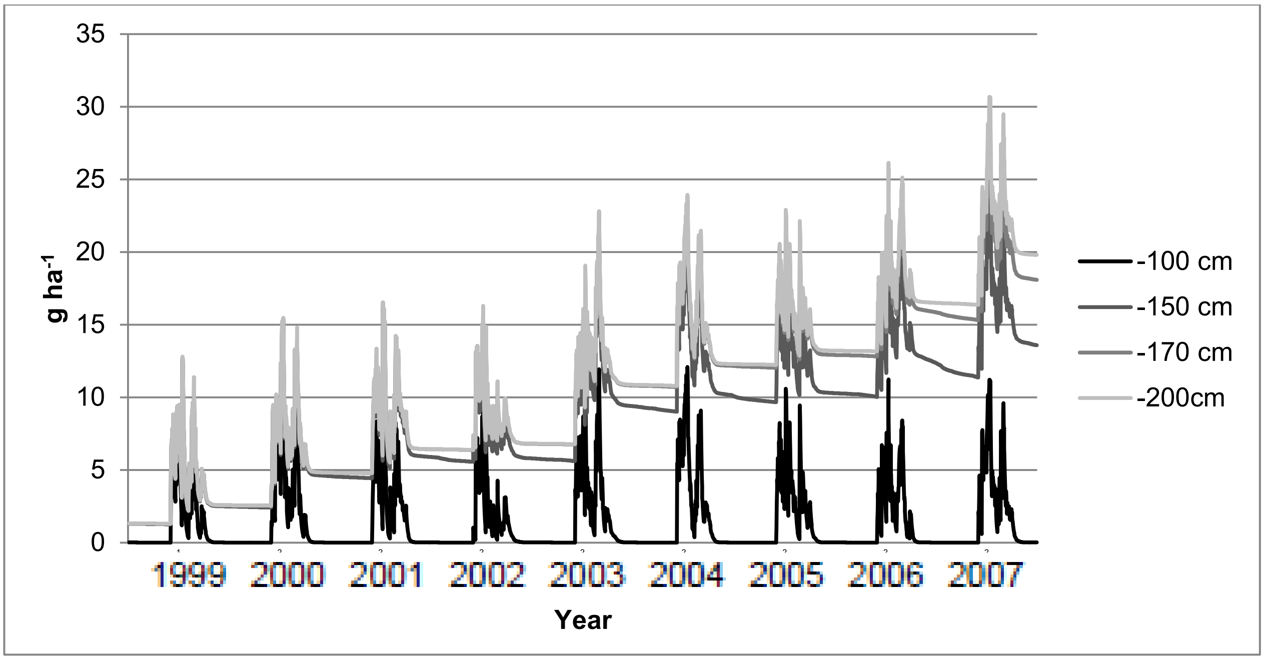
Drained artemisinin concentration over the whole simulation period (1999- 2007) in the sandy loam soil for scenario 1. The presented concentrations are daily snap-shots.

The figure below shows the artemisinin balance in the whole sandy loam soil profile where most of the infiltrating artemisinin ('In') is getting degraded each subsequent spring. Although only hardly visible in the figure, the leaching concentration is accumulating in 200 cm soil depth from 1.4 * 10^{-18} g m^{-3} in 1999 to 3.7 * 10^{-8} g m^{-3} in 2007. The content is accumulating with the highest peak of 19.8 g ha^{-1} in 2007. Preferential flow is as well occurring to a soil depth of 150 cm in irregular intervals ranging from 3.2 * 10^{-5} g m^{-3} in 1999 to 3.2 * 10^{-4} g m^{-3} in 2003. The same is true for drainage within a range between 3.2 * 10^{-10} g m^{-3} in 1999 and 1.0 * 10^{-6} g m^{-3} in 2007 where artemisinin purges to the next adjacent water body.



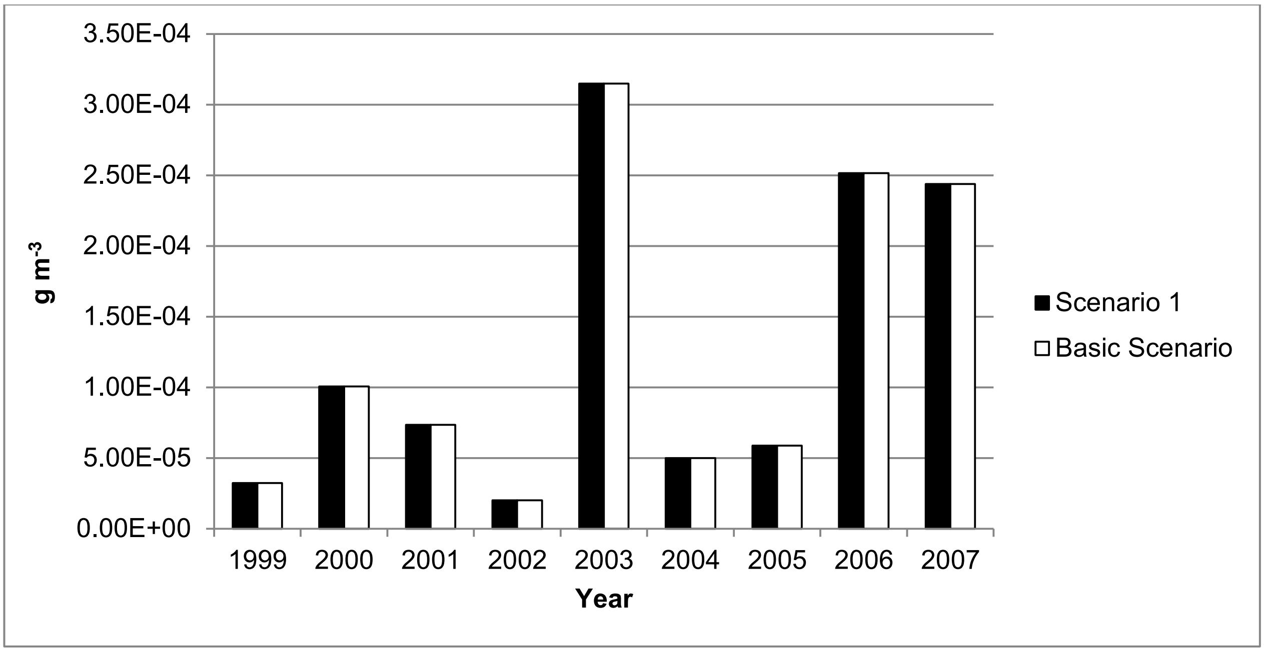
Simulated artemisinin balance in the sandy loam soil for scenario 1 within the whole soil profile (0-200 cm) and for all simulated years. It is consisting of the infiltration ('In'), leaching until 200 cm depth, preferential flow in 150 cm depth, drainage and degradation which are all annual sums (concentration considered to be mass per volume soil system). The content is the simulated on a daily snap-shot basis on the last day of each year.

According to the figure below all artemisinin gets fully degraded from 0 to 100 cm depth until each subsequent spring and is accumulated afresh on the 1st of June. In a soil depth from 150 cm to 200 cm artemisinin gets accumulated. The highest accumulating amount 50 cm above the groundwater is 1.71 g ha^{-1} and occurs in the year 2007. An erratic fluctuation is observed each year with the highest peak in 2007 of about 30 g ha^{-1} and between 0 and 200 cm soil depth.



Artemisinin content trend in the sandy loam soil for scenario 1 over the whole measuring period (1999- 2007) and four different soil depths. The accumulated content is made up of the difference between trend- lines.

The figure below reveals that there are no differences for the preferential flow concentrations between scenario 1 and the basic scenario over the whole simulation period.

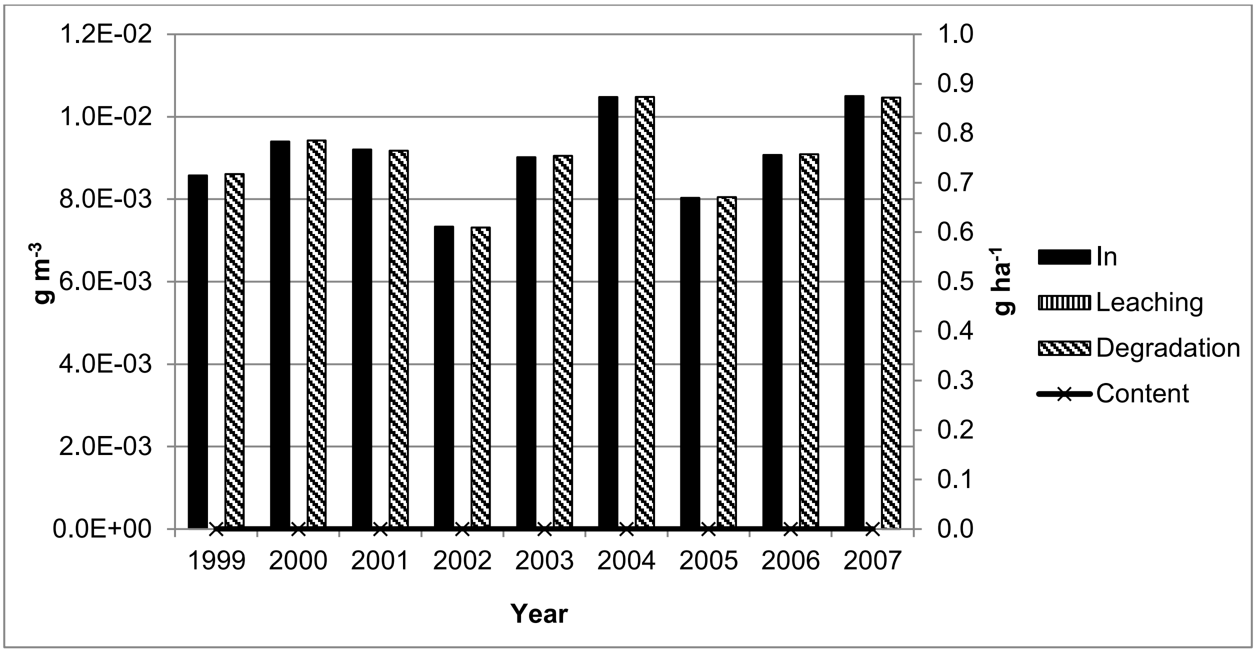


Preferential flow comparison between the Scenario 1 (DT50 4.3) and the basic scenario (DT50 8.3) over the whole simulation period (1999-2007). The concentrations are calculated as annual sums (mass per volume soil system).

XIII Scenario 2 extra figures

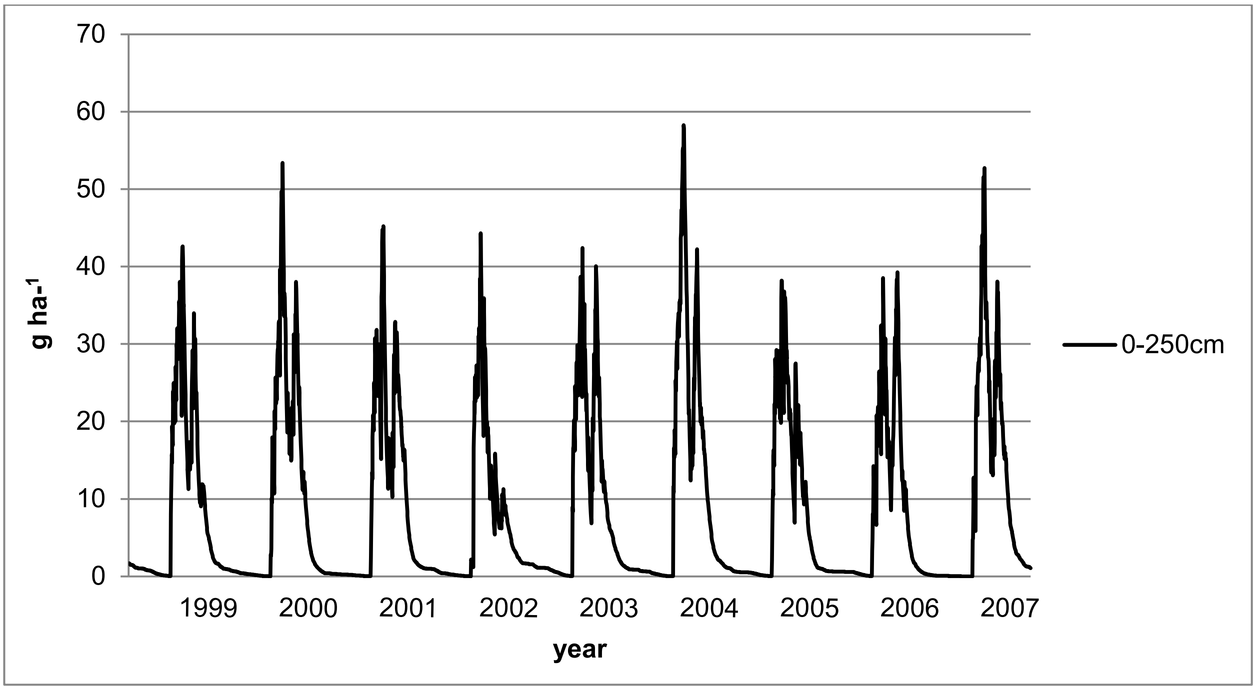
XIII.I Sandy soil

The figure below shows the artemisinin balance in the whole sandy soil profile where all the infiltrating artemisinin ('In') is getting degraded each subsequent spring. No leaching below 95 cm depth is occurring and therefore as well no accumulation.



Artemisinin balance in the sandy soil for scenario 2 within the whole soil profile (0- 250 cm) and all simulated years. It is consisting of the infiltration ('In'), leaching and degradation which are all annual sums (concentration considered to be mass per volume soil system). The content is the simulated daily snap-shot on the last day of each year.

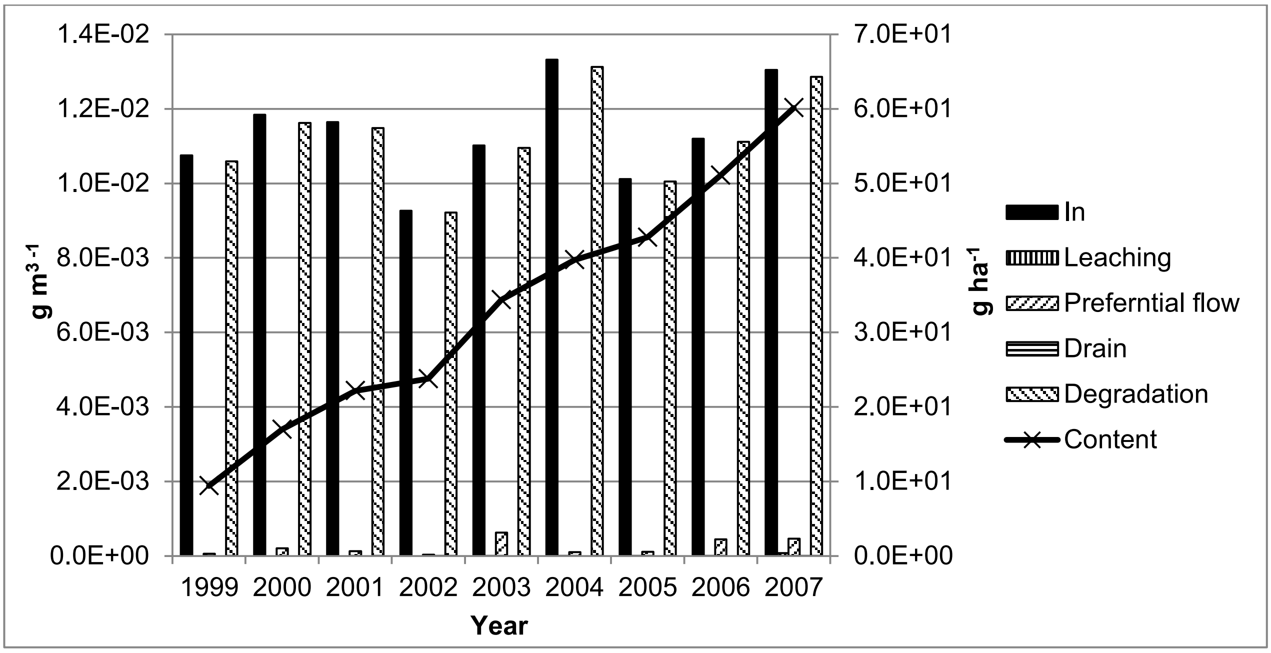
According to the figure below all artemisinin gets fully degraded until each subsequent spring and is accumulated afresh on the 1st of June. An erratic fluctuation is observed each year with the highest content peak of about 59 g ha^{-1} in 2004.



Artemisinin content trend over the entire simulation period (1999- 2007) for scenario 2 and the whole soil profile (0- 250 cm).

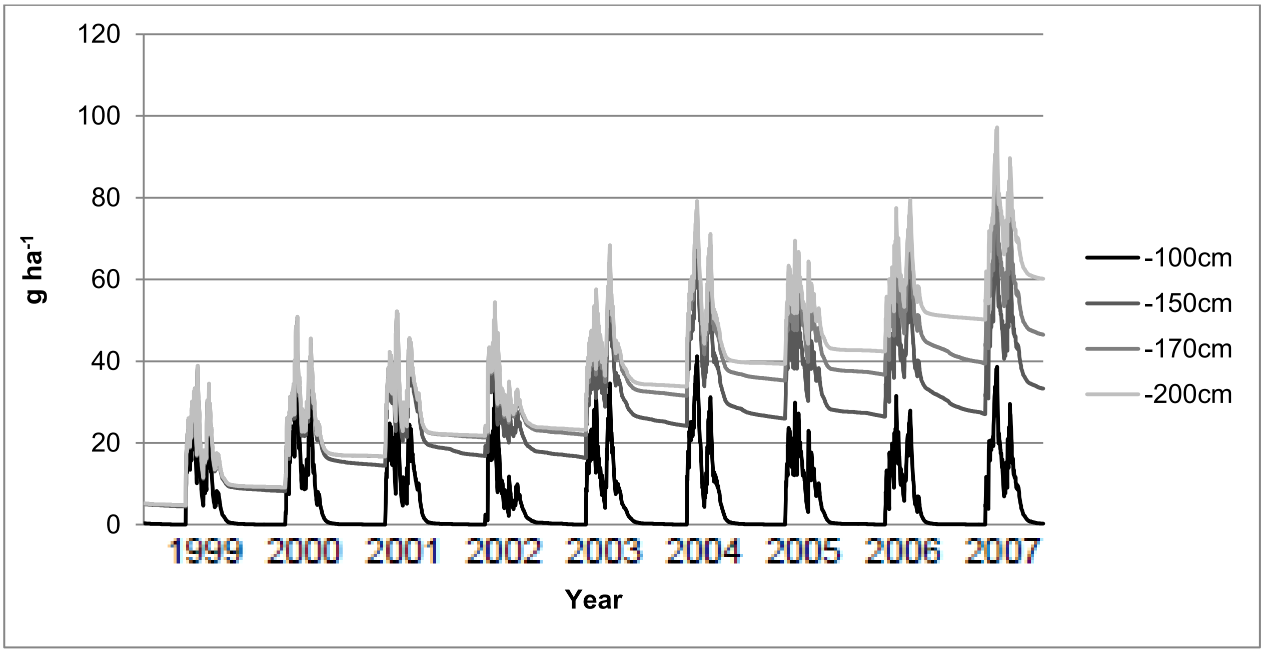
XIII.II Sandy loam soil

The figure below reveals the artemisinin balance in the whole sandy loam soil profile for scenario 2 where most of the infiltrating artemisinin ('In') is getting degraded each subsequent spring. Although not visible in the figure, the leaching concentration is accumulating in 200 cm soil depth from 9.4 * 10^{-13} g ha^{-1} in 1999 to 1.44 g ha^{-1} in 2007. The content is correspondingly accumulating with the highest peak of 60.1 g ha^{-1} in 2007. Preferential flow is as well occurring to a soil depth of 150 cm in irregular intervals ranging from 0.86 g ha^{-1} in 1999 to 9.35 g ha^{-1} in 2003. The same is true for drainage within a range between 4.99 g 10^{-5} ha-1 in 1999 and 0.114 g ha^{-1} in 2007 where artemisinin purges to the next adjacent water body.



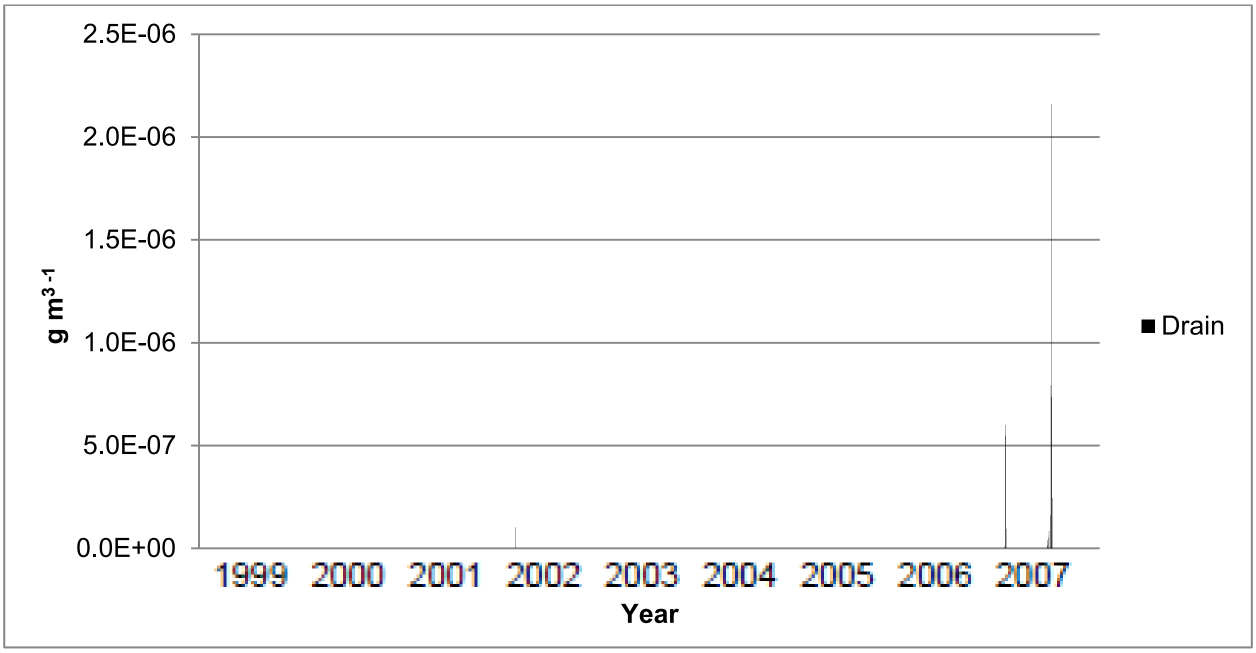
Artemisinin balance in the sandy loam soil for scenario 2 within the whole soil profile (0- 200 cm) and all simulated years. It is consisting of the infiltration ('In'), leaching in 200 cm depth, preferential flow in 150 cm depth, drainage and degradation which are all annual sums. The content is on a daily snap-shot basis on the last day of each year.

In the figure below all artemisinin gets fully degraded from 0 to 100 cm depth until each subsequent spring and is accumulated afresh on the 1st of June. In a soil depth from 150 cm to 200 cm artemisinin gets accumulated. The highest accumulating amount 50 cm above the groundwater is 13.6 g ha-1 and occurs in the year 2007. An erratic fluctuation is observed each year with the highest peak in 2007 in a of about 95 g ha^{-1}.



Artemisinin content trend in the sandy loam soil for scenario 2 over the whole measuring period (1999- 2007) and four different soil depths. The accumulated content is made up of the difference between trend- lines.

Drainage of artemisinin is presented in the figure below and reveals a fluctuating pattern. The drained concentration ranges from 7.6 * 10^{-6} g m^{-3} to 4.3 * 10^{-2} g m^{-3} both in 2007.



Drained artemisinin concentration over the whole simulation period (1999- 2007) for scenario 2. The presented concentrations are daily snap-shots.

XIV Ecotoxicological assessment

XIV.I Basic scenario sandy soil

The table represents the average concentration that is reaching the upper groundwater in the sandy soil for the basic scenario. All the values are simulated within 250 cm soil depth.

Year	Annual percolation (mm)	Annual percolation (m^3 ha^{-1} $year^{-1}$)	Leaching (g ha^{-1} $year^{-1}$)	Average concentration (g m^{-3})	Average concentration (mg L^{-1})
1999	747	7470	$7.79 * 10^{-15}$	- [a]	-
2000	750	7500	$1.08 * 10^{-14}$	-	-
2001	601	6010	$8.21 * 10^{-15}$	-	-
2002	940	9400	$6.27 * 10^{-15}$	-	-
2003	502	5020	$8.61 * 10^{-15}$	-	-
2004	776	7760	$1.00 * 10^{-14}$	-	-
2005	546	5460	$7.60 * 10^{-15}$	-	-
2006	810	8100	$7.90 * 10^{-15}$	-	-
2007	1107	11070	$8.19 * 10^{-15}$	-	-

[a] considered to be zero.

XIV.II Basic scenario sandy loam soil

The table represents the average concentration that is reaching the upper groundwater in the sandy loam soil for the basic scenario. All the values are simulated within 200 cm soil depth.

Year	Annual percolation (mm)	Annual percolation (m^3 ha^{-1} $year^{-1}$)	Leaching (g ha^{-1} $year^{-1}$)	Average concentration (g m^{-3})	Average concentration (mg L^{-1})
1999	330	3300	$6.52 * 10^{-14}$	$1.97 * 10^{-17}$	$1.97 * 10^{-17}$
2000	284	2840	$2.89 * 10^{-13}$	$1.02 * 10^{-16}$	$1.02 * 10^{-16}$
2001	274	2740	$5.87 * 10^{-12}$	$2.14 * 10^{-15}$	$2.14 * 10^{-15}$
2002	388	3880	$1.60 * 10^{-9}$	$4.12 * 10^{-13}$	$4.12 * 10^{-13}$
2003	259	2590	$1.82 * 10^{-8}$	$7.03 * 10^{-12}$	$7.03 * 10^{-12}$
2004	246	2460	$2.70 * 10^{-7}$	$1.1 * 10^{-10}$	$1.1 * 10^{-10}$
2005	255	2550	$4.16 * 10^{-6}$	$2.3 * 10^{-9}$	$2.3 * 10^{-9}$
2006	312	3120	$1.38 * 10^{-4}$	$4.4 * 10^{-8}$	$4.4 * 10^{-8}$
2007	541	5410	$1.15 * 10^{-2}$	$2.13 * 10^{-6}$	$2.13 * 10^{-6}$

The table represents the content accumulation per year from 170cm to 200cm soil depth for the basic scenario.

Year	Annual percolation (mm)	Annual percolation (m^3 ha^{-1} $year^{-1}$)	Content accumulation (g ha^{-1} $year^{-1}$)	Average concentration (g m^{-3})	Average concentration (mg L^{-1})
1999	330	3300	$2.0 * 10^{-5}$	$6 * 10^{-9}$	$6 * 10^{-9}$
2000	284	2840	$3.3 * 10^{-4}$	$1.16 * 10^{-7}$	$1.16 * 10^{-7}$
2001	274	2740	$4.4 * 10^{-3}$	$1.6 * 10^{-6}$	$1.6 * 10^{-6}$
2002	388	3880	$5.6 * 10^{-2}$	$1.44 * 10^{-5}$	$1.44 * 10^{-5}$
2003	259	2590	$1.6 * 10^{-1}$	$6.16 * 10^{-5}$	$6.16 * 10^{-5}$
2004	246	2460	$3.6 * 10^{-1}$	$1.46 * 10^{-4}$	$1.46 * 10^{-4}$
2005	255	2550	$7.2 * 10^{-1}$	$2.82 * 10^{-4}$	$2.82 * 10^{-4}$
2006	312	3120	1.4	$4.48 * 10^{-4}$	$4.48 * 10^{-4}$
2007	541	5410	3.3	$6.09 * 10^{-4}$	$6.09 * 10^{-4}$

The table represents drained concentration leading to the next stream or lake in the basic scenario for the sandy loam soil. Within the simulation period, only in 1999, 2002, and 2007 drainage of artemisinin occurred.

Year	Annual drained percolation (mm)	Annual drained percolation (m^3 ha^{-1} year^{-1})	Drain (g ha^{-1} year^{-1})	Average drained concentration (g m^{-3})	Average drained concentration (mg L^{-1})
1999	0.22	2.2	$1.23 * 10^{-5}$	$5.59 * 10^{-6}$	$5.59 * 10^{-6}$
2002	0.85	8.5	$5.31 * 10^{-4}$	$6.27 * 10^{-5}$	$6.27 * 10^{-5}$
2007	12	120	$3.21 * 10^{-2}$	$2.68 * 10^{-4}$	$2.68 * 10^{-4}$

XIV.III Scenario 1 sandy loam soil

The table represents the average concentration that is reaching the upper groundwater in the sandy loam soil for scenario 1. All the values are simulated within 200 cm soil depth.

Year	Annual percolation (mm)	Annual percolation (m^3 ha^{-1} year^{-1})	Leaching (g ha^{-1} year^{-1})	Average concentration (g m^{-3})	Average concentration (mg L^{-1})
1999	330	3300	$2.69 * 10^{-14}$	$8.15 * 10^{-18}$	$8.15 * 10^{-18}$
2000	284	2840	$6.65 * 10^{-14}$	$2.3 * 10^{-17}$	$2.3 * 10^{-17}$
2001	274	2740	$8.08 * 10^{-13}$	$2.95 * 10^{-16}$	$2.95 * 10^{-16}$
2002	388	3880	$1.82 * 10^{-10}$	$4.7 * 10^{-14}$	$4.7 * 10^{-14}$
2003	259	2590	$1.28 * 10^{-9}$	$4.94 *10^{-13}$	$4.94 *10^{-13}$
2004	246	2460	$1.44 * 10^{-8}$	$5.85 * 10^{-12}$	$5.85 * 10^{-12}$
2005	255	2550	$1.46 * 10^{-7}$	$5.73 * 10^{-11}$	$5.73 * 10^{-11}$
2006	312	3120	$4.59 * 10^{-6}$	$1,3 * 10^{-9}$	$1,3 * 10^{-9}$
2007	541	5410	$7.40 * 10^{-4}$	$1.37 * 10^{-7}$	$1.37 * 10^{-7}$

The table represents the content accumulation per year from 170cm to 200cm soil depth for scenario 1.

Year	Annual percolation (mm)	Annual percolation (m^3 ha^{-1} year^{-1})	Content accumulation (g ha^{-1} year^{-1})	Average concentration (g m^{-3})	Average concentration (mg L^{-1})
1999	330	3300	0.0	0.0	0.0
2000	284	2840	$7.00 * 10^{-5}$	$2.5 * 10^{-8}$	$2.5 * 10^{-8}$
2001	274	2740	$1.04 * 10^{-3}$	$3.8 * 10^{-7}$	$3.8 * 10^{-7}$
2002	388	3880	$1.58 * 10^{-2}$	$4.07 * 10^{-6}$	$4.07 * 10^{-6}$
2003	259	2590	$5.10 * 10^{-2}$	$1.96 * 10^{-5}$	$1.96 * 10^{-5}$
2004	246	2460	$1.30 * 10^{-1}$	$5.28 * 10^{-5}$	$5.28 * 10^{-5}$
2005	255	2550	$2.93 * 10^{-1}$	$1.14 * 10^{-4}$	$1.14 * 10^{-4}$
2006	312	3120	$6.50 * 10^{-1}$	$2.08 * 10^{-4}$	$2.08 * 10^{-4}$
2007	541	5410	1.71	$3.16 * 10^{-4}$	$3.16 * 10^{-4}$

The table represents drained concentration leading to the next stream or lake for scenario 1 for the sandy loam soil. Within the simulation period, only in 1999, 2002, and 2007 drainage of artemisinin occurred.

Year	Annual drained percolation (mm)	Annual drained percolation (m^3 ha^{-1} year^{-1})	Drain (g ha^{-1} year^{-1})	Average drained concentration (g m^{-3})	Average drained concentration (mg L^{-1})
1999	0.22	2.2	$6.31 * 10^{-6}$	$2.86 * 10^{-6}$	$2.86 * 10^{-6}$

2002	0.85	8.5	$3.11 * 10^{-4}$	$3.65 * 10^{-5}$	$3.65 * 10^{-5}$
2007	12	120	$2.05 * 10^{-2}$	$1.71 * 10^{-4}$	$1.71 * 10^{-4}$

XIV.IV Scenario 2 sandy soil

The table represents the average concentration that is reaching the upper groundwater in the sandy soil for scenario 2. All the values are simulated within 250 cm soil depth.

Year	Annual percolation (mm)	Annual percolation (m^3 ha^{-1} year^{-1})	Leaching (g ha^{-1} year^{-1})	Average concentration (g m^{-3})	Average concentration (mg L^{-1})
1999	747	7470	$1.87 * 10^{-14}$	- [a]	-
2000	750	7500	$2.48 * 10^{-14}$	-	-
2001	601	6010	$1.95 * 10^{-14}$	-	-
2002	940	9400	$1.6 * 10^{-14}$	-	-
2003	502	5020	$1.73 * 10^{-14}$	-	-
2004	776	7760	$2.47 * 10^{-14}$	-	-
2005	546	5460	$1.83 * 10^{-14}$	-	-
2006	810	8100	$2.08 * 10^{-14}$	-	-
2007	1107	11070	$2.69 * 10^{-14}$	-	-

[a] considered to be zero

XIV.V Scenario 2 sandy loam soil

The table represents the average concentration that is reaching the upper groundwater in the sandy loam soil for scenario 2. All the values are simulated within 200 cm soil depth.

Year	Annual percolation (mm)	Annual percolation (m^3 ha^{-1} year^{-1})	Leaching (g ha^{-1} year^{-1})	Average concentration (g m^{-3})	Average concentration (mg L^{-1})
1999	330	3300	$9.44 * 10^{-13}$	$2.86 * 10^{-16}$	$2.86 * 10^{-16}$
2000	284	2840	$2.17 * 10^{-11}$	$7.64 * 10^{-15}$	$7.64 * 10^{-15}$
2001	274	2740	$1.69 * 10^{-9}$	$6.17 * 10^{-13}$	$6.17 * 10^{-13}$
2002	388	3880	$1.63 * 10^{-6}$	$4.2 * 10^{-10}$	$4.2 * 10^{-10}$
2003	259	2590	$8.01 * 10^{-5}$	$3.1 * 10^{-8}$	$3.1 * 10^{-8}$
2004	246	2460	$1.74 * 10^{-3}$	$7.07 * 10^{-7}$	$7.07 * 10^{-7}$
2005	255	2550	$1.81 * 10^{-2}$	$7.09 * 10^{-6}$	$7.09 * 10^{-6}$
2006	312	3120	$1.5 * 10^{-1}$	$4.81 * 10^{-5}$	$4.81 * 10^{-5}$
2007	541	5410	1.43	$2.64 * 10^{-4}$	$2.64 * 10^{-4}$

The table represents the content accumulation per year from 170cm to 200cm soil depth for scenario 2.

Year	Annual percolation (mm)	Annual percolation (m^3 ha^{-1} year^{-1})	Content accumulation (g ha^{-1} year^{-1})	Average concentration (g m^{-3})	Average concentration (mg L^{-1})
1999	330	3300	$4.90 * 10^{-4}$	$1.48 * 10^{-7}$	$1.48 * 10^{-7}$
2000	284	2840	$1.05 * 10^{-2}$	$3.69 * 10^{-6}$	$3.69 * 10^{-6}$
2001	274	2740	$1.12 * 10^{-1}$	$4.08 * 10^{-5}$	$4.08 * 10^{-5}$
2002	388	3880	$8.34 * 10^{-1}$	$2.14 * 10^{-4}$	$2.14 * 10^{-4}$
2003	259	2590	1.75	$6.75 * 10^{-4}$	$6.75 * 10^{-4}$
2004	246	2460	3.10	$1.26 * 10^{-3}$	$1.26 * 10^{-3}$
2005	255	2550	5.08	$1.99 * 10^{-3}$	$1.99 * 10^{-3}$
2006	312	3120	8.15	$2.6 * 10^{-3}$	$2.6 * 10^{-3}$

2007	541	5410	13.6	$2.51 * 10^{-3}$	$2.51 * 10^{-3}$

The table represents drained concentration leading to the next stream or lake in scenario 2 for the sandy loam soil. Within the simulation period, only in 1999, 2002, and 2007 drainage of artemisinin occurred.

Year	**Annual drained percolation (mm)**	**Annual drained percolation (m^3 ha^{-1} $year^{-1}$)**	**Drain (g ha^{-1} $year^{-1}$)**	**Average drained concentration (g m^{-3})**	**Average drained concentration (mg L^{-1})**
1999	0.22	2.2	$4.99 * 10^{-5}$	$2.26 * 10^{-5}$	$2.26 * 10^{-5}$
2002	0.85	8.5	$2.13 * 10^{-3}$	$2.5 * 10^{-4}$	$2.5 * 10^{-4}$
2007	12	120	$1.14 * 10^{-1}$	$9.5 * 10^{-4}$	$9.5 * 10^{-4}$

XV Simulation set up for the sandy soil and basic scenario

```
;;; artemisinin.dai --- Environmental impact assessment.

(input file "vegetation.dai")
(input file "chemistry-base.dai")
(input file "dk-soil.dai")
(input file "log.dai")

;; We use "base" pesticide values that are surely wrong.
;; Jyndevad horizon Ap 0-30 cm(0.038 clay, 0.072 silt, 0.867 sand, 0.023 humus) according to daisy lib
;; Jyndevad horizon C 30cm- 250cm(0.028 clay, 0.023 silt, 0.945 sand, 0.004 humus) according to daisy lib
(defchemical Artemisinin common
  (decompose_halftime 13.5 [d])
  ;; Freundlich sorption.
  (adsorption Freundlich
        (K_OC 41.94 [(mg/L)^-m])
        (m 0.4491 [])))

;; No reactions beside instant equilibrium sorption and decomposition.
(defchemistry Artemisinin default
  (trace Artemisinin))

;; We model Artemisia annua after permanent grass.
;; Main error here is likely that we then pretent there is a static root zone.
(defvegetation Artemisia_annua Grass
;; Julian day vs. LAI. CHANGE!
(LAIvsDAY (147 0.0)
        (224 1.0)
        (315 5.0)
        (322 0.0)))

;; Artemisia release cycle.
(defaction Release activity
  ;; Yearly cycle.
  (repeat (activity
       ;; Do nothing before 1. June.
       (wait_mm_dd 06 01 (hour 1))

       ;; Release... g/ha until 15. June.
       (while (wait_mm_dd 06 15 (hour 1))
         (repeat  (activity                                                  .
              (spray_surface Artemisinin 1.8355 [g/ha])
              (wait daily))))
       (wait_period (hours 1)(days 1))

      ;; Release ... g/ha until 1. July.
                        (while (wait_mm_dd 07 01 (hour 1))
                          (repeat (activity
                               (spray_surface Artemisinin 1.5699 [g/ha])
                               (wait daily))))
       (wait_period (hours 1)(days 1))

      ;; Release ... g/ha until 15. July.
                        (while (wait_mm_dd 07 15 (hour 1))
                          (repeat (activity
                                                (spray_surface Artemisinin 3.0293 [g/ha])
                                                (wait daily))))
       (wait_period (hours 1)(days 1))
      ;; Release ... g/ha until 1. August.
                        (while (wait_mm_dd 08 01 (hour 1))
                          (repeat (activity
                                                (spray_surface Artemisinin 0.8748 [g/ha])
                               (wait daily))))
                        (wait_period (hours 1)(days 1))

      ;; Release ... g/ha until 15. August
       (while (wait_mm_dd 08 15 (hour 1))
         (repeat  (activity
              (spray_surface Artemisinin 0.7586 [g/ha])
              (wait daily))))
       (wait_period (hours 1)(days 1))

      ;; Release ... g/ha until 01. September.
       (while (wait_mm_dd 09 01 (hour 1))
         (repeat (activity
              (spray_surface Artemisinin 2.2985 [g/ha])
              (wait daily))))
       (wait_period (hours 1)(days 1))

       ;; Release ... g/ha until 15. September.
       (while (wait_mm_dd 09 15 (hour 1))
```

```
                                    (repeat (activity
                                                      (spray_surface Artemisinin 0.55 [g/ha])
                          (wait daily))))
                     (wait_period (hours 1)(days 1))

                     ;; Release ... g/ha until 01. October.
                                  (while (wait_mm_dd 10 01 (hour 1))
                                   (repeat (activity
                                                      (spray_surface Artemisinin 0.5037 [g/ha])
                           (wait daily))))))
                                 (wait_period (hours 1)(days 1)))

          ;; Release 100 g/ha 16. October.
           ;;spray Artemisinin 100 [g/ha]

;; Common information for the two sites.
(defcolumn Base default
  ;; As previously defined.
 (Vegetation Artemisia_annua)
  (Chemistry multi (combine Artemisinin))
  ;; Ignore N and C cycles.
  (OrganicMatter none))

(defprogram Base Daisy
  ;; Artemisinin release.
  (manager Release)
  ;; Hourly weather data from Taastrup.
  (weather default "dk-taastrup-hourly.dwf"
                                              (PrecipScale 2.18 2.19 1.96 1.21 1.22 1.28 1.36 1.29 1.14 1.80 1.66 2.09))

;  (activate_output
(after (1998 04 01)))
  (stop 2008 04 01)
  ;; output files
  (output
  ;; We log total balance, top 1 meter, top 1.5 meter (just at the macropore ending), top 1.7 meter (just above the groundwater and below the macropores),
and top 2 meters.
                                 ("Field chemical" (chemical Artemisinin) (when hourly) (where "hourly_field_Artemisinin"))
          ("Field chemical" (chemical Artemisinin) (when daily) (where "daily_field_Artemisinin"))
          ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -1 [m]) (when hourly) (where "hourly_soil-Artemisinin-1m"))
          ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -1 [m]) (when daily) (where "daily_soil-Artemisinin-1m"))
          ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -1.5 [m]) (when hourly) (where "hourly_soil-Artemisinin-1.5m"))
          ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -1.5 [m]) (when daily) (where "daily_soil-Artemisinin-1.5m"))
          ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -1.7 [m]) (when hourly) (where "hourly_soil-Artemisinin-1.7m"))
          ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -1.7 [m]) (when daily) (where "daily_soil-Artemisinin-1.7m"))
          ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -2 [m]) (when hourly) (where "hourly_soil-Artemisinin-2m"))
          ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -2 [m]) (when daily) (where "daily_soil-Artemisinin-2m"))
          ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -2.5 [m]) (when hourly) (where "hourly_soil-Artemisinin-2.5m"))
          ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -2.5 [m]) (when daily) (where "daily_soil-Artemisinin-2.5m"))
  ;; Water balance 0-100 cm
                                 ("Soil water" (to -100 [cm])(when daily)(where "Daily_WB-100cm.dlf"))
                                 ("Soil water" (to -100 [cm])(when monthly) (where "Monthly_WB-100cm.dlf"))
  ;; Water balance 0-150 cm
                                 ("Soil water" (to -150 [cm])(when daily)(where "Daily_WB-150cm.dlf"))
                                 ("Soil water" (to -150 [cm])(when monthly) (where "Monthly_WB-150cm.dlf"))
  ;; Water balance 100-200 cm
                                 ("Soil water" (to -200 [cm])(when daily)(where "Daily_WB-200cm.dlf"))
                                 ("Soil water" (to -200 [cm])(when monthly) (where "Monthly_WB-200cm.dlf"))
  ;; Water balance 100-250 cm
                                 ("Soil water" (to -250 [cm])(when daily)(where "Daily_WB-250cm.dlf"))
                                 ("Soil water" (to -250 [cm])(when monthly) (where "Monthly_WB-250cm.dlf"))
  ;; Soil profile data
          ("Soil Water Content"       (when daily) (where "SWC_daily"))
          ("Soil Water Potential (pF)"(when daily) (where "SWP_daily"))))

;; Jyndevad soil.
;; Source: Daisy sample directory.
(defcolumn jyn Base
  (Groundwater deep)
  (Soil (MaxRootingDepth 60 [cm])
        (horizons (  -30.00 "Jyndevad Ap")
                  ( -250.00 ("Jyndevad C" (humus 1.4 [%]))))))

(defprogram Jyndevad Base
  (log_prefix "jyn-")
  (column jyn))
  ;; Run simulation.
(defprogram both batch
  (run Jyndevad))
(run both)
;;; artemisinin.dai ends here.
```

XVI Simulation set up for the sandy loam soil and basic scenario

```
;;; artemisinin.dai --- Environmental impact assessment.

(input file "vegetation.dai")
(input file "chemistry-base.dai")
(input file "dk-soil.dai")
(input file "log.dai")

;; We use "base" pesticide values that are surely wrong.
;; Taastrup horizon Ap 3-25cm (0.107 clay, 0.222 silt, 0.671 sand, humus 0.03)according to daisy lib
;; Taastrup horizon B 33-120 cm(0.222 clay, 0.195 silt, 0.583 sand, humus 0.016)according to daisy lib

(defchemical Artemisinin common
  (decompose_halftime 8.3 [d])
  ;; Freundlich sorption.
  (adsorption Freundlich
        (K_OC 32.92 [(mg/L)^-m])
        (m 0.5998 [])))

;; No reactions beside instant equilibrium sorption and decomposition.
(defchemistry Artemisinin default
  (trace Artemisinin))

;; We model Artemisia annua after permanent grass.
;; Main error here is likely that we then pretent there is a static root zone.
(defvegetation Artemisia_annua Grass
;; Julian day vs. LAI. CHANGE!
(LAIvsDAY (147 0.0)
        (224 1.0)
        (315 5.0)
        (322 0.0)))

;; Artemisia release cycle.
(defaction Release activity
  ;; Yearly cycle.
  (repeat (activity
        ;; Do nothing before 1. June.
        (wait_mm_dd 06 01 (hour 1))
        ;; Release ... g/ha until 15. June.
        (while (wait_mm_dd 06 15 (hour 1))
          (repeat  (activity
                (spray_surface Artemisinin 1.8355 [g/ha])
                (wait daily))))
        (wait_period (hours 1)(days 1))

       ;; Release ... g/ha until 1. July.
                        (while (wait_mm_dd 07 01 (hour 1))
                          (repeat (activity
                                (spray_surface Artemisinin 1.5699 [g/ha])
                                (wait daily))))
        (wait_period (hours 1)(days 1))

       ;; Release ... g/ha until 15. July.
                        (while (wait_mm_dd 07 15 (hour 1))
                                (repeat (activity
                                        (spray_surface Artemisinin 3.0293 [g/ha])
                                        (wait daily))))
        (wait_period (hours 1)(days 1))

        ;; Release ... g/ha until 1. August.
                        (while (wait_mm_dd 08 01 (hour 1))
                          (repeat (activity
                                        (spray_surface Artemisinin 0.8748 [g/ha])
                                (wait daily))))
                        (wait_period (hours 1)(days 1))

        ;; Release ... g/ha until 15. August
        (while (wait_mm_dd 08 15 (hour 1))
          (repeat  (activity
                (spray_surface Artemisinin 0.7586 [g/ha])
                (wait daily))))
                        (wait_period (hours 1)(days 1))

        ;; Release ... g/ha until 01. September.
        (while (wait_mm_dd 09 01 (hour 1))
          (repeat (activity
                (spray_surface Artemisinin 2.2985 [g/ha])
                (wait daily))))
        (wait_period (hours 1)(days 1))

        ;; Release ... g/ha until 15. September.
```

```
        (while (wait_mm_dd 09 15 (hour 1))
                          (repeat (activity
                                                  (spray_surface Artemisinin 0.55 [g/ha])
               (wait daily))))
         (wait_period (hours 1)(days 1))

         ;; Release ... g/ha until 01. October.
                          (while (wait_mm_dd 10 01 (hour 1))
                          (repeat (activity
                                                   (spray_surface Artemisinin 0.5037 [g/ha])
               (wait daily)))))))

        ;; Release 100 g/ha 16. October.
        ;;spray Artemisinin 100 [g/ha]

;; Common information for the two sites.
(defcolumn Base default
  ;; As previously defined.
 (Vegetation Artemisia_annua)
  (Chemistry multi (combine Artemisinin))
  ;; Ignore N and C cycles.
  (OrganicMatter none))

(defprogram Base Daisy
  ;; Artemisinin release.
  (manager Release)
  ;; Hourly weather data from Taastrup.
  (weather default "dk-taastrup-hourly.dwf")
  (time 1997 08 01)
  (activate_output
  (after (1998 04 01)))
  (stop 2008 04 01)
  ;; output files
  (output
  ;; We log total balance, top 1 meter, top 1.5 meter (just at the macropore ending), top 1.7 meter (just above the groundwater and below the macropores),
and top 2 meters.
                        ("Field chemical" (chemical Artemisinin) (when hourly) (where "hourly_field_Artemisinin"))
        ("Field chemical" (chemical Artemisinin) (when daily) (where "daily_field_Artemisinin"))
        ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -1 [m]) (when hourly) (where "hourly_soil-Artemisinin-1m"))
        ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -1 [m]) (when daily) (where "daily_soil-Artemisinin-1m"))
        ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -1.5 [m]) (when hourly) (where "hourly_soil-Artemisinin-1.5m"))
        ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -1.5 [m]) (when daily) (where "daily_soil-Artemisinin-1.5m"))
        ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -1.7 [m]) (when hourly) (where "hourly_soil-Artemisinin-1.7m"))
        ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -1.7 [m]) (when daily) (where "daily_soil-Artemisinin-1.7m"))
        ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -2 [m]) (when hourly) (where "hourly_soil-Artemisinin-2m"))
        ("Soil chemical" (chemical Artemisinin) (from 0 [cm]) (to -2 [m]) (when daily) (where "daily_soil-Artemisinin-2m"))
  ;; Water balance 0-100 cm
                        ("Soil water" (to -100 [cm])(when daily)(where "Daily_WB-100cm.dlf"))
                        ("Soil water" (to -100 [cm])(when monthly) (where "Monthly_WB-100cm.dlf"))
  ;; Water balance 0-150 cm
                        ("Soil water" (to -150 [cm])(when daily)(where "Daily_WB-150cm.dlf"))
                        ("Soil water" (to -150 [cm])(when monthly) (where "Monthly_WB-150cm.dlf"))
  ;; Water balance 100-200 cm
                        ("Soil water" (to -200 [cm])(when daily)(where "Daily_WB-200cm.dlf"))
                        ("Soil water" (to -200 [cm])(when monthly) (where "Monthly_WB-200cm.dlf"))
  ;; Soil profile data
        ("Soil Water Content"      (when daily) (where "SWC_daily"))
        ("Soil Water Potential (pF)"(when daily) (where "SWP_daily"))))

;; Taastrup soil
;;
;; Source: MST-VAP project.
(defhorizon "Taastrup Ap" USDA3
  (clay 0.107) (silt 0.222) (sand 0.671) (humus 0.03)
  (dry_bulk_density 1.49 [g/cm^3]))

(defhorizon "Taastrup Surface" "Taastrup Ap"
  (hydraulic original ;; 10%
          (K_sat 0.173704 [cm/h])))

(defhorizon "Taastrup plow pan" USDA3
  (clay 0.148)(silt 0.214)(sand 0.638) (humus 0.016)
  (dry_bulk_density 1.70 [g/cm^3])
  (anisotropy 12)
  (hydraulic M_vG (Theta_res 0.00)
             (Theta_sat 0.339353 )
             (alpha 0.0465371)
             (n 1.19395)
             (K_sat (* 0.5 [] 0.0925 [cm/h]))
             (l -2.92948)))

(defhorizon "Taastrup Bt" USDA3
  (clay 0.222)(silt 0.195)(sand 0.583)(humus 0.016)
```

```
  (dry_bulk_density 1.65 [g/cm^3])
  (hydraulic M_vG (Theta_res 0.0)
                (l -4.0323)
                (n 1.14768)
                (alpha 0.0565146)
                (K_sat (* 0.5 [] 0.537042 [cm/h]))
                (Theta_sat 0.356969)))

(defhorizon "Taastrup C" USDA3
  (clay 0.207)(silt 0.235)(sand 0.558) (humus 0.01)
  (dry_bulk_density 1.69 [g/cm^3])
  (hydraulic M_vG (Theta_res 0.000)
                (Theta_sat 0.348314)
                (alpha 0.0476257)
                (n 1.15336)
                (K_sat 1.50000 [cm/h])
                (l -3.60322)))

(defcolumn "taa" Base
  (Soil (MaxRootingDepth 150 [cm])
        (horizons (-3.00 "Taastrup Surface")
                (-25.00 "Taastrup Ap")
                (-33.00 "Taastrup plow pan")
                (-120 "Taastrup Bt")
                (-200 "Taastrup C")))
  (Drain lateral)
  (Groundwater aquitard
              (K_aquitard 0.050 [cm/h])
              (Z_aquitard 200 [cm])))

(defprogram Taastrup Base
  (log_prefix "taa-")
  (column taa))

;; Run simulation.

(defprogram both batch
  (run Taastrup))

(run both)

;;; artemisinin.dai ends here.
```