

FATE OF PESTICIDES

- IN AGRICULTURAL SOILS

CHRISTEN DUUS BØRGESEN, INGE S. FOMSGAARD, FINN PLAUBORG, KIRSTEN SCHELDE
AND NIELS HENRIK SPLIID

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Preface

The present review was financed by the AU Integration project funds that facilitated the integration of specific research interests at Agroecology Flakkebjerg and Agroecology Foulum. The report reviews state-of-art modelling concepts of fate of pesticides in agricultural soils, focusing on Danish conditions. The report presents new areas of research that are needed to better understand transport processes at various scales and to develop new models, e.g. catchment scale models for estimating the risk of loss of pesticides/contaminants to the environment.

Aarhus Universitet, Foulum, 2015

Christen Duus Børgesen, Inge S. Fomsgaard, Finn Plauborg, Kirsten Schelde, and Niels Henrik Spliid

1. Introduction

An increasing interest for studying the fate of pesticides when applied in agricultural cropping systems was observed in Denmark in the last decades of the twentieth century. In that period the Danish Environmental Protection Agency (DEPA) focused on pesticide losses to both ground and surface waters and in 1989 a programme to survey and research the mobility of pesticides was initiated. Spliid and Mogensen (1995) investigated leaching of 11 herbicides and some degradation products from two small catchments - one with a subsurface consisting of sandy soils and one with clayey soils. At both catchments crops were grown in a traditional crop rotation. The leaching risk of herbicides and degradation products was monitored by sampling and analysing water from two soil water stations, two drainage systems, and two streams. The main findings were that all herbicides analysed for were found in leachate from the clayey catchment with a more intense spraying than in the sandy catchment. The herbicides were mostly found during the spraying season in spring, but also when heavy rains were observed in the autumn. The monitoring in the less intensely cultivated sandy catchment generally revealed fewer findings of different herbicides and at lower concentrations.

The Danish National Groundwater Monitoring Programme (GRUMO) revealed the presence of pesticides and their degradation products in approx. 30% of the monitored screens (GEUS, 2000), and serious doubts were raised at DEPA as to whether the present approval procedure for pesticides was adequate. Hence, in 1998, the Danish Parliament initiated the Danish Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions (e.g. Kjær et al., 2011a). The Danish Government funded the first phase of the programme from 1998 to 2001. The programme has been prolonged twice, initially with funding from the Ministry of the Environment and the Ministry of Food, Agriculture and Fisheries for the period 2002 to 2009, and presently with funding from the Danish Environmental Protection Agency for the period 2010 to 2015. The programme currently evaluates the leaching risk of 42 pesticides and 41 degradation products at five agricultural sites ranging in size from 1.1 to 2.4 ha (Kjær et al., 2011a). The monitoring programme was designed to detect if the annual average concentration of pesticides and their degradation products in water lost from the root zone would, individually, exceed $0.1 \mu\text{g L}^{-1}$; the limit corresponding to the quality criterion of current drinking water legislation.

The present study presents state-of-the-art description of transport and fate of pesticides (especially herbicides as they are by far the most used) when applied in the agricultural landscape, as presented in Fig. 1.1. The main focus will be on the description of sorption and degradation and the transport of pesticides to ground water and surface waters. Pesticide leaching loss to the aquatic environment is strongly regulated by Danish Water regulations and the Water Framework Directive (tolerating an annual maximum average concentration of $0.1 \mu\text{g L}^{-1}$), however also other pathways for loss will be discussed.

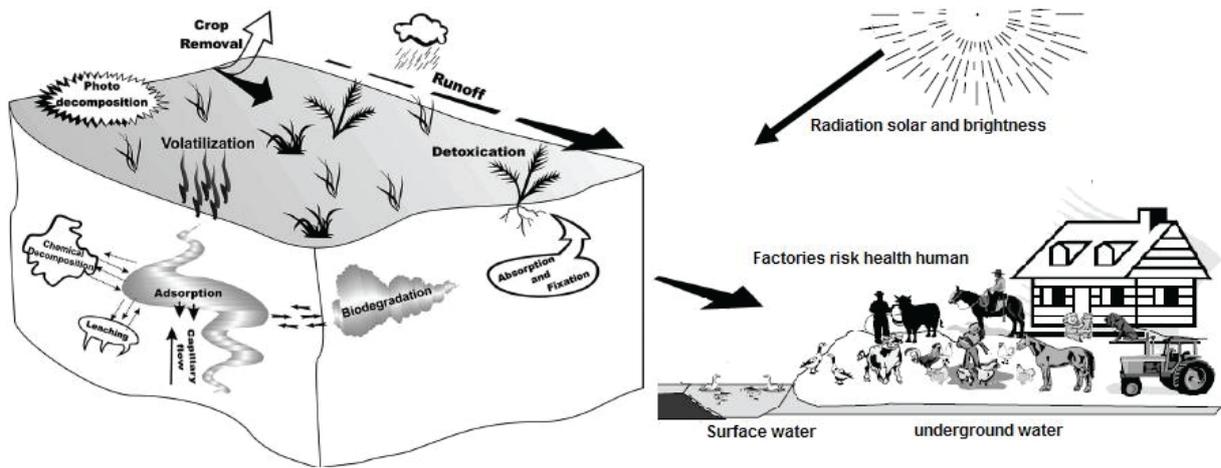


Figure 1.1. Pesticides in the environment (Cardeal, 2011; based on Strandberg et al., 1998, and adapted by Bavcon et al., 2002).

Finally, the present work will briefly present main knowledge gaps related to flow and transport of pesticides and present a catalogue of new research ideas.

2. Adsorption and desorption

2.1 Chemical bonds

Sorption of pesticides is based on two phenomena, weak chemical bonds and diffusion of the compound into the soil structure. Diffusion in the water phase into the capillaries is a physical process, where the compound is still in the liquid phase, but “hanging” in capillaries meaning that measurements of the concentration in the aqueous phase will be without the contribution from the part trapped in the soil structure. Diffusion is reversible and the compound will contribute to the equilibration in a desorption study. Reversible sorption based on chemical bonds can be caused by the ionic properties of the compound. Phenols and organic acids will be adsorbed to positive sites of the soil surface, and positive compounds like quaternary amines will be adsorbed to negative sites. Hydrogen bonds are weaker bonds, where the electropositive protons of a chemical compound will stick to electronegative atoms on the soil surface and vice versa. Chemical reactions between the compound and sites in the soil resulting in covalent bonds will in general represent irreversible sorption where the chemical is built into the humic acid structure of the soil.

2.2 Concepts

Sorption of pesticides to soil influences the mobility and risk for contamination of the soil and water environment. Non-sorbing compounds will conservatively follow the water movement while a sorbing compound will be retained depending on the sorption properties. The degree of sorption depends on the properties of the compound, the soil properties and the properties of the water phase.

For comparison of sorption properties of different compounds, international guidelines have been developed and mutually recognized for test of adsorption and desorption (*OECD guideline for testing of chemicals: Adsorption – Desorption Using a Batch Equilibrium Method*. No. 106, adopted 21 January, 2000).

The method is a batch shaking method where the distribution of the compound between soil and soil water is determined. For soil water 10 mM calcium chloride is used. The soil can be a well described reference soil if the purpose is to estimate the sorption properties of a given compound. In that case it will be relevant to include a known compound for reference purposes. Alternatively, the study can be performed with a well known compound to test a specific soil with unknown sorption properties. The sorption properties are given as a K_d -value that is the ratio between the concentration of sorbed compound on the soil and the concentration in the soil water:

$$K_d = C_s / C_{aq}$$

A high K_d value means high sorption to soil and vice versa. A K_d -value is given as $L\ kg^{-1}$ or $cm^3\ g^{-1}$.

For general comparison of sorption properties of different compounds independent of the soil used for the study, the K_d -value can be recalculated to a K_{oc} -value. K_{oc} is the ratio between the concentration of

sorbed compound to the organic carbon fraction of the soil (C_{oc}) and the concentration in the soil water (C_{aq}). If the organic carbon content of the soil is 1% and the K_d -value has been determined to 1.5, the K_{oc} -value will be 150 L kg^{-1} . The prerequisite for this calculation is that the entire amount of sorbed compound is sorbed to the carbon fraction. For some compounds like glyphosate such a calculation will lead to erroneous results, since glyphosate can be sorbed to the inorganic minerals in the soil as well as to the organic fraction. (Glass, 1987)

Equilibrium. In general equilibrium of the compound between soil and water will be reached relatively fast. To be sure that the equilibrium has been reached in the K_d -study, the K_d -value has to be determined after 4, 8, and 24 hours, eventually also after 48 hours. Normally, equilibrium has already been reached after 4 hours.

Concentration. With increasing concentration some of the active sites, to which the compound will be sorbed, might be saturated. This means that K_d can decrease with increasing concentration. The concentration effect is taken into account using the Freundlich adsorption constant, K_f . The Freundlich isotherm is defined by

$$c_s = K_f * c^n$$

where:

c_s = concentration in solid phase,

c = concentration in fluid phase,

K_f = Freundlich adsorption constant,

n = Freundlich exponent.

If $n = 1$, the Freundlich isotherm reduces to the linear isotherm independent of concentration.

2.3 Desorption

Desorption can be determined in the same way as adsorption is determined. After finalization of the adsorption study, the soil water is removed and substituted with soil water not containing the compound. The concentration in the water phase is determined after a period of 24 and 48 hours. If the process is reversible and if no degradation has occurred, and if the adsorption isotherm is linear, the K_d -values calculated for adsorption and desorption should be the same. Trapping of the compound in the soil structure or varied bond mechanisms may result in a delayed desorption leading to a different dynamic desorption profile than the adsorption profile (hysteresis).

2.4 Examples

The resulting sorption is a result of the different sorption processes, which can involve different mechanisms at the different moieties of the molecule. Fluazifop-buthyl is an ester, so the acidic part is masked and this gives a high K_d -value. The Footprint database

(<http://sitem.herts.ac.uk/aeru/footprint/en/index.htm>) states a value of 41 L kg⁻¹. Fluazifop-butyl easily dissociates to the fluazifop free acid with a $K_d = 7.1 \text{ L kg}^{-1}$ according to the Footprint database. The K_d -value highly depends on the content of soil organic carbon, why K_d -values determined with soil from the A-horizon generally will be much higher than for sub soils with a lower organic carbon content. The sorption of glyphosate is very much dependent on the occurrence of metal ions and the presence of minerals. The www.Pesticiddata.dk database gives 27 different K_d -values for glyphosate ranging from 5.3 to 24000 L kg⁻¹s determined in different trials.

3. Degradation

3.1 Introduction

The degradation of a pesticide in soil can take place through chemical or microbiological processes. Often one or more steps take place chemically (e.g. a hydrolysis) while the following steps are microbiological. The chemical degradation processes come to an end relatively quickly so the microbiological processes become the more interesting subject to study. The degradation generally happens gradually through the formation of one or more metabolites. By a total degradation of a chemical, CO₂, salts, and water are formed, and parts of the chemical are built into new molecular structures in the soil humus or in biomass. As an example of a complex degradation pathway Fig. 3.1 shows a schematic picture of the degradation of the fungicides maneb and mancozeb (Fomsgaard et al., 1998)

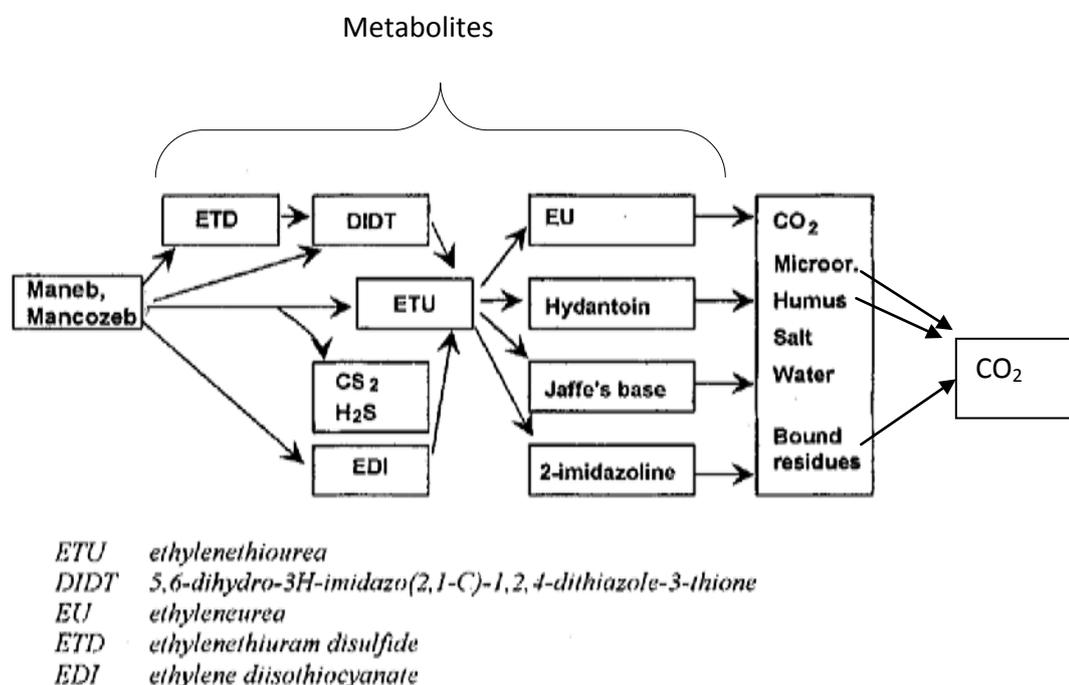


Fig. 3.1. Schematic presentation of the degradation of the fungicides maneb and mancozeb (Fomsgaard et al., 1998).

Microbial degradation can progress metabolically – that is microorganisms using the substances that are being degraded for growing – or it can progress co-metabolically where the substances are degraded by microorganisms that are unable to use pesticide as a source of energy or nourishment. In the metabolic degradation process the degradation rate of the substance is increased as the microorganisms are growing.

Traditional research into the degradation of pesticides is often performed in batch experiments in the laboratory where the influence of other processes such as leaching or volatilization are eliminated. In such traditional batch experiments, the soil is mixed and homogenized by sieving before using it in the experiment. Degradation studies have been presented where small undisturbed samples were collected in tubes and the pesticide was added by suction (Fomsgaard, et al., 1998). The advantage of using the mixed soil samples is the relative ease of handling many samples and the reduced variation in the results, while the advantage of using undisturbed samples is that the degrading microorganisms are in an environment similar to the natural environment (Johannesen et al, 1996)

Recently attempts have been made to determine degradation rates of pesticides in column experiments using mathematical models for determining sorption, degradation and leaching concurrently, as for instance Matallo et al. (2005). The study used the multi-layered AF (Attenuation Factor) model for predicting the herbicides leaching in undisturbed soil columns in which sorption and degradation models were included.. The AF model was able to predict leaching amounts in the sandy soil, especially for diuron, however it did not perform well in the clayey soil.

When ^{14}C -labelled pesticides are used for degradation experiments, the formation of ^{14}C -labelled CO_2 is measured and depicted as shown in Fig. 3.2. The complete degradation to CO_2 is a mineralization process.

When un-labelled pesticides are used for degradation experiments, the amount of pesticide that is left in soil is extracted and analyzed in liquid chromatography coupled to a detector (mass spectrometric instruments being the most sensitive) and depicted as a function of days, as for instance shown in Fig. 3.3.

Many factors influence the degradation of pesticides in soil. Here we may list factors such as the structure of the compound, temperature, water content, soil texture, microbiological activity, the composition of the other organic matter of the soil, the soil microbial biomass, the biological diversity, plant coverage, and soil depth. The depth of the soil influences the degradation rate of pesticides because of the spatially very variable chemical and biological conditions. All the individual factors affecting pesticide degradation rates and pathways can be attributed to one of the following four groups: 1. Intrinsic properties of the pesticide; 2. The soil and its characteristics; 3. The climate; 4. The method and the amounts in which the compound is applied.

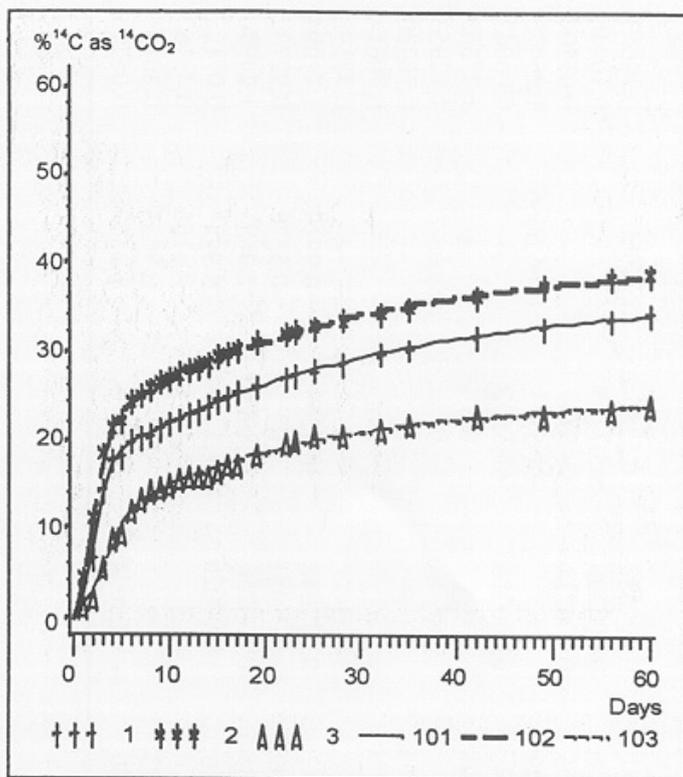


Fig. 3.2. Mineralisation of ¹⁴C-ETU in soil described as %¹⁴C of added ¹⁴C-ETU evolved as ¹⁴CO₂ as a function of time. Study performed on soil samples from the plough layer; concentration of added ¹⁴C-ETU 0.07 μg g⁻¹; temperature 5°C (Fomsgaard and Kristensen, 1999). Three replicates. Datapoint labelled 1, 2 and 3. Mathematical model labelled 101, 102 and 103.

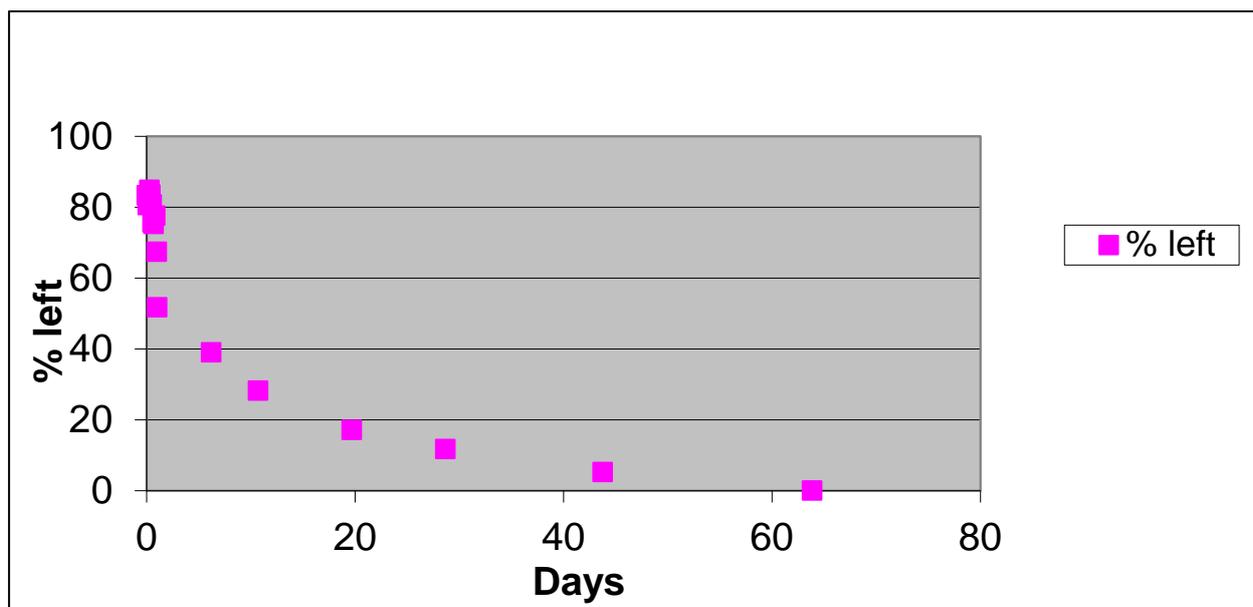


Fig. 3.3. Typical degradation curve from a degradation experiment using un-labelled pesticide (Fomsgaard, unpublished).

3.2 Degradation kinetics

Pesticide degradation was described using simple 1st order kinetics (SFO) for many decades, and first order kinetics is still the most common mathematical description of pesticide degradation in the literature. The reasons for this are many:

1. Experience:
 - a. Shows that in fact many abiotic and biotic processes in the environment (e.g. soil) follow SFO.
2. It is practical:
 - a. The equation is simple and contains only two parameters.
 - b. It is normally easy to fit an equation to the experimental data.
 - c. It is easy to calculate DT_{50} or DT_{90} (or read from a semi-logarithmic plot of the data).
 - d. The parameters are independent of the concentration and thus a simple first order degradation equation is easy to use in leaching models.
3. Scientifically sound:
 - a. Abiotic hydrolytic processes generally follow SFO.
 - b. Biotic degradation processes at the concentration levels at which pesticides are used may generally be considered as 1st order processes because the responsible microorganisms – or enzymes – are always present in excess compared to the number

of molecules to be degraded. Thus the chemical compound, - the pesticide – is the only limiting factor for degradation.

The SFO model is expressed as:

$$C = C_0 e^{-kt}$$

$$\frac{dC}{dt} = -kC$$

where C = amount of pesticide present at time t , k = rate constant for the degradation process, and C_0 = amount of pesticide at time 0 (initial amount).

In spite of the many reasons for using SFO for describing degradation kinetics, reality often shows that the SFO is *not* acceptable. Fig. 3.4 shows an example where the use of SFO results in a good fit, and Fig. 3.5 shows an example where the SFO results in a bad fit. Fits should be evaluated according to several criteria: a) visual inspection of the curve; b) evaluation of the distribution of residuals (should be homogeneous); c) Degrees of freedom (DF) adjusted r^2 close to 1; d) parameter values should be logical and confidence interval should not embrace 0.

On the basis of the visual inspection (data points deviate from model curve), evaluation of residuals (non-homogenous distribution and DF adjusted $r^2 = 0.93$ the SFO fit of Compound 2 must be discarded (Fig. 3.5).

An expert group, supported by the European Commission (2003-2006) developed procedures for finding alternative kinetic equations for describing pesticide degradation (Work Group on Degradation Kinetics of FOCUS - FOrum for the Co-ordination of pesticide fate models and their USE) (Boesten et al., 2006).

The FOCUS degradation kinetics expert group came up with two alternative equations for pesticide degradation in soil; - alternatives that are based on 1st order kinetics, but composed of several 1st order processes. The alternative equations are the First Order Multi Compartment (FOMC) equation and the Double First Order in Parallel equation (DFOP) (Fig. 3.6 and 3.7).

Equation	$C = C_0 e^{-kt}$ (Single First Order, SFO)			
Curve				
Residuals				
DF adjusted r2	0.9871			
Parameter values	Parameter	Value	Std. error	95 %Confidence Limits
	C0	103.0245	3.0215	96.0567 - 109.9923
	k	0.05047	0.00341	0.04260 - 0.05835
DT50	13.7 days			
DT90	45.6 days			

Fig. 3.4. SFO fit to "Compound 1" dataset.

Equation	$C = C_0 e^{-kt}$ (Single First Order, SFO)			
Curve				
Residuals				
DF adjusted r ²	0.9385			
	Parameter	Value	Std. error	95 %Confidence Limits
Parameter values	C_0	88.6604	5.6331	75.3401 - 101.9806
	k	0.09400	0.01708	0.05360 - 0.13440
DT ₅₀	7.37 days			
DT ₉₀	24.50 days			

Fig. 3.5. SFO fit to “Compound 2” data.

The First Order Multi Compartment equation (FOMC) is expressed as:

$$C = C_0 \left(\frac{t}{\beta} + 1 \right)^{-\alpha}$$

where C = amount of pesticide at time t , C_0 = amount of pesticide at time 0 , β = parameter determined by the variation in k values, and α = positional parameter.

The Double First Order in Parallel (DFOP) equation is expressed as:

$$C = C_1 e^{-k_1 t} + C_2 e^{-k_2 t}$$

where C = amount of pesticide present at time t , C_1 = amount of pesticide at time 0 in the first compartment, k_1 = rate constant for degradation in the first compartment, C_2 = amount of pesticide at time 0 in the second compartment, and k_2 = rate constant for degradation in the second compartment.

Alternative equations for describing a biological process should rely on a mechanistic understanding of the process. The FOMC model, proposed by Gustafson and Holden (1990) and adapted by the FOCUS group on degradation kinetics, has a mechanistic background. Soil is a heterogeneous medium so it is likely that degradation often occurs at different rates within individual regions of the soil sample under investigation. This is accounted for in the model by dividing the soil into a large number of sub-compartments, each with a different first order degradation rate constant. If the distribution of rate coefficients is described by a gamma-distribution, this results in a simple analytical equation with three parameters.

A fast initial decrease in pesticide concentrations is often followed by a slower decline. Thus another relevant alternative model is the DFOP or the bi-phasic model. There are several possible mechanistic reasons for this phenomenon: Scow (1993) hypothesises that only the fraction of pesticide in soil solution is available for degradation. The available fraction often decreases with time due to slow sorption and diffusion processes (Pignatello, 2000). This may decrease the rate of degradation of pesticide at later stages of the experiment. Non-linear sorption with Freundlich exponents <1 results in decreasing availability of pesticide in soil solution with decreasing concentrations. If only dissolved pesticide is available for degradation, a fast initial decrease in pesticide concentrations will be followed by a slower decline.

Equation	$C = C_0 \left(\frac{t}{\beta} + 1 \right)^{-\alpha}$ <p>(also named First Order Multi Compartment, FOMC)</p>			
Curve				
Residuals				
DF adjusted r2	0.9918			
	Parameter	Value	Std. error	95 %Confidence Limits
Parameter values	C0	97.0616	2.5963	90.7085 - 103.4148
	β	4.2192	1.1578	1.3860 - 7.0524
	α	0.9186	0.1326	0.5941 - 1.2430
DT50	4.75 days			
DT90	47.52 days			

Fig. 3.6. FOMC fit to "Compound 2" data.

Equation	$C = C_1e^{-k_1t} + C_2e^{-k_2t}$ (Double First Order in Parallel equation, DFOP)			
Curve				
Residuals				
DF adjusted r2	0.9883			
	Parameter	Value	Std. error	95 %Confidence Limits
Parameter values	C1	48.7771	7.91586	28.42871 - 69.12544
	K1	0.41078	0.12173	0.09786 - 0.72370
	C2	48.76873	7.83672	28.623806 - 68.91367
	K2	0.09400	0.01708	0.05360 - 0.13440
DT50	4.48 days			
DT90	41.80 days			

Fig. 3.7. DFOP fit to “Compound 2” data.

The results of using the FOMC model and the DFOP model for description of the degradation kinetics of compound 2 are seen in Fig. 3.6 and Fig. 3.7, respectively. Both FOMC and DFOP are much better models for Compound 2 than the SFO model. This is seen by visual inspection of the curve, in the residuals, and in the DF adjusted r^2 . When choosing between FOMC and DFOP, visual inspection of the curves and the residuals do not provide a basis for a decision. The DF adjusted r^2 is slightly better for the FOMC model. The parameters for the DFOP model however reveal a very broad confidence interval. The parameters also reveal that apparently the two compartments were determined to have exactly the same size in terms of amount of compound (48 in C_1 and C_2). This is unlikely to occur and thus FOMC is the preferred model. In case the evaluation ended up pointing to FOMC and DFOP as equally suitable models, FOMC would be the model of choice as it is the simplest model with the least parameters.

A comparison of the determined DT50 and DT90 values using the SFO and the FOMC model, respectively, shows that a serious error would occur if the SFO model was chosen by mistake for Compound 2. The DT90 value according to the FOMC model is 48 days. Using the SFO model, DT90 would be determined to 25 days.

In some cases results from pesticide degradation studies show a virtually constant concentration for an initial period of time, followed by a first-order decline in pesticide concentration. The initial phase is referred to as lag-phase (Boesten et al, 2006). In some cases this can be attributed to experimental artefacts in laboratory trials. In such cases the lag phase is omitted from the kinetic studies. A true lag-phase can be caused by slow adaptation of degrading microorganisms or by an inhibitory action of high concentrations of pesticides on the degrading microorganisms. In such cases Boesten et al (2006) recommends to use either a sequential model or a logistic model.

3.3 Dealing with alternative degradation kinetics when using the MACRO leaching model

Two possible procedures were outlined by the FOCUS work group on degradation kinetics (Boesten et al., 2006) aiming at explicitly considering bi-phasic degradation in PEC calculations (*predicted environmental concentrations*). The implementation of the FOMC and the DFOP model into soil models simulating transport of parent compounds and their metabolites to ground and surface water (PEARL, PELMO, PRZM, MACRO, and TOXSWA) is not universally valid. There are, however, approaches that provide a pragmatic solution. The first approach provided in the guideline (Boesten et al., 2006) is based on the assumption that the observed bi-phasic degradation pattern is caused by kinetic sorption (i.e. a decrease in the easily degradable fraction of pesticide with time). Parameters for mathematical descriptions of long-term sorption and concurrent degradation are calculated from parameters derived by fitting empirical bi-phasic kinetics to degradation data. The calculated parameters are then used for higher-tier simulations with leaching models. The second approach consists of two pragmatic techniques to implement bi-exponential degradation kinetics into pesticide leaching models.

4. Water flow and transport of pesticide at point to field scale

This section reviews the processes for transport of pesticides in soils at small local scales: pedon, soil cores, soil monoliths, and field. The following refers to recent studies and review papers on the theory for flow, model development, and new understanding of processes involved. The understanding of processes at local scale is important for understanding transport at higher scales (field, catchments), which is addressed in a later section focusing on scaling concepts, e.g., aggregation (based on effective parameters) or real scaling (deriving new scale dependent processes and parameters).

Depending on their mobility and persistence, pesticides can migrate within and outside the soil and contaminate water and air. The main pesticide transfer processes are a) atmospheric: spray drift, volatilisation, and atmospheric transport followed by re-deposition, or b) water-driven: drainage, leaching, and surface and subsurface runoff. The relative importance of each of the processes depends on the pesticide application conditions, the pesticide properties, the climatic conditions, and the soil properties partly governed by agricultural practices (Alletto et al., 2010; Reichenberger, 2007). Most pesticide transfer processes have a diffuse-source nature, but point sources in the form of farmyard runoff, accidental spills, or sewer outflows can also cause significant contamination of water bodies with pesticides.

During pesticide application by spraying, a certain portion of the applied amount may be deposited outside the target area, e.g. on untargeted soil, plant, and water surfaces. The extent of spray drift losses depend on weather conditions, application method and equipment, and the target crop. In contrast to most other pesticide losses, the spray drift losses are independent of the pesticide properties (Reichenberger et al., 2007). Spray drift can lead to high, yet short-lived, levels of exposure in receiving water bodies. However, simulations by Huber et al. (2000) and Röpke et al. (2004) suggested that total spray drift inputs to surface waters in Germany are much lower than inputs by surface runoff or drainage.

Volatilisation of pesticides is controlled by the pesticide properties (saturated vapour pressure, Henry constant, K_{oc} etc.), the soil properties (soil structures, water content, organic carbon contents etc.), the climate conditions (wind, radiation, temperature etc.), and the farming practices (mode of pesticide application, soil roughness, possible layer of mulch etc.) (Bedos et al., 2002).

Pesticide sorption is enhanced under conservation tillage since crop residues residing in or above the soil have sorption capacities 10 to 60 times higher than soil (Alletto et al., 2010). Pesticide retention is generally positively correlated with organic carbon content which is increased in the top soil under conservation tillage (Alletto et al., 2010). Greater proportions of pesticide remain sorbed on soil particles and on mulch under conservation tillage. As a consequence, a lower fraction of pesticide remains available for biological degradation under conservation tillage and pesticide persistence in the soil may increase (Alletto et al., 2010). However, increased content of organic carbon (OC) may

increase the microbial activity and then even accelerate the degradation of pesticides (Fomsgaard, 2004). These conditions demonstrate that the potential for pesticide leaching may be estimated as the total amount of adsorbed pesticide, especially as the in situ degradation parameters may not be well determined. Hence, in simulation models it is quite normal to apply lab determined degradation parameters, derived from sieved soils under static conditions; conditions that may be quite different from processes in reality (Beulke and Brown, 2001).

Pesticide leaching through the unsaturated zone to ground water is a complex process controlled by soil and environmental conditions. Pesticide leaching is highest for weakly sorbing and/or persistent compounds, for climates with high precipitation and low temperatures leading to high groundwater recharge, and for soils with either 1) sandy texture and low organic matter, promoting leaching by matrix flow, or 2) soils promoting macropore flow, e.g. heavy loams and clays (Reichenberger et al., 2007).

In the soil matrix, solutes move by convection-dispersion and, due to good contact between the liquid and solid phases, the opportunities for pesticide retention in the soil are greater than in macropores. In preferential flow, water and solutes bypass the matrix and allow a downward flow at a higher rate than if movement occurred in the matrix only. Bypass flow may occur during saturated or near-saturated conditions (Jarvis 2007), but is also found in media much drier than saturation and can occur in pores that are incompletely filled (Nimmo, 2012; Rosenbom et al. 2008, 2009a). Preferential flow is heterogeneous and intermittent in nature, and therefore difficult to predict. Travel times for pesticides preferentially leached are comparable to those of conservative tracers or solutes, with losses of typically less than 1% of the applied dose, but reaching up to 5% of the applied mass (Köhne et al., 2009b).

Drainage (water flow to and in tile drains) is often a rather event-based process while leaching is more continuous in nature (Reichenberger et al. 2007). This is mainly due to the typical soils where drainage and leaching predominate: Drained soils are usually fine-textured, clayey soils exhibiting a peaky, event-driven behaviour, while a predominance of leaching to groundwater is often associated with somewhat lighter soils where matrix transport plays a more significant role.

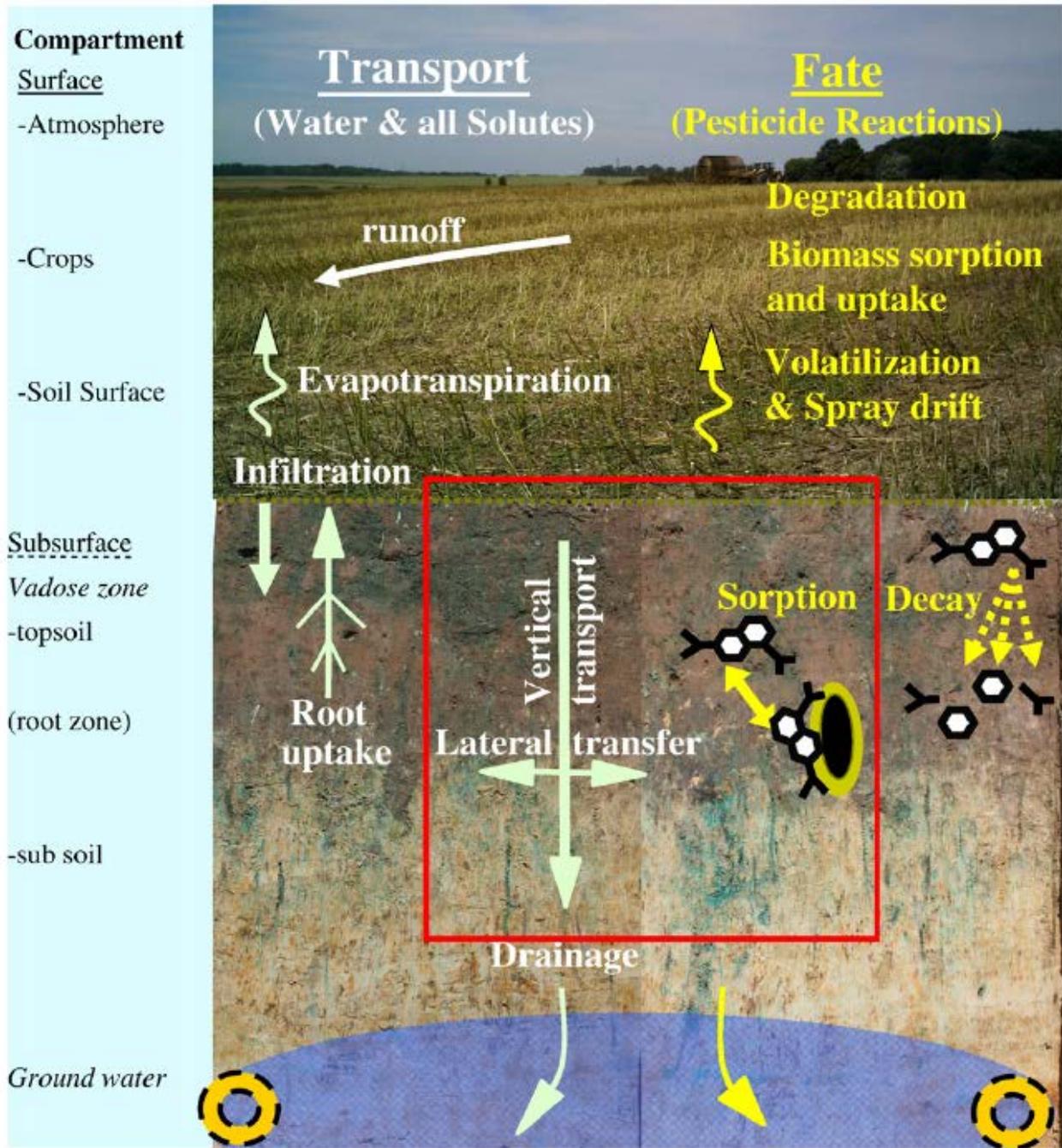


Figure 4.1. Processes governing pesticide transport and fate in agricultural structured soils (from Köhne et al., 2009b).

4.1 Matrix and preferential flow

To fully describe flow and transport of pesticides, nutrients, etc. a complete understanding of the flow of soil water at small scales is needed; either flow only in the soil matrix or combined flow in the macropore system and in the soil matrix. Chapters 2 and 3 describe processes affecting the fate of pesticides in soils, i.e. degradation, adsorption/desorption etc. These processes have a major effect on the possible transport of the pesticide through the vadose zone to ground water and/or drainage water.

Variably-saturated water flow through the soil matrix can be described by Richard's equation

$$\frac{\partial \theta}{\partial h} \frac{\partial h}{\partial t} = \frac{\partial}{\partial z} \left(k(h) \frac{\partial h}{\partial z} - 1 \right)$$

where θ is volumetric water content, h is soil water pressure [L], t is time [T], and z the vertical coordinate [L].

Few analytical solutions to this equation exist and only for special boundaries, e.g. soil water infiltration and bare soil evaporation. Hence the equation is most often solved based on a numerical representation and defined parameter functions, e.g. the water retention curve and saturated/unsaturated hydraulic conductivity. In addition upper and lower boundaries need to be described. The upper boundary (at the soil surface) is then precipitation input and water loss by evapotranspiration. At the bottom the condition may vary (e.g. free drainage, fixed hydraulic head).

The parameters in such a system have validity only within the scale of measurement, and it is well known from field studies that rather high spatial variation in parameter values may be found, e.g. the uncertainty on the saturated hydraulic conductivity in coarse sand was found to be more than three orders of magnitude (Jacobsen, 1989).

Solute transport can be described with Convection Dispersion Equation (CDE) (e.g. Vanderborght, 2007).

$$\theta \frac{\partial C}{\partial t} + \rho_b \frac{\partial S}{\partial t} = -\theta v \frac{\partial C}{\partial z} + \frac{\partial}{\partial z} \left(\theta D \frac{\partial C}{\partial z} \right) - F(C, S)$$

where θ is the volumetric water content, C [M L⁻³] the concentration in soil water, ρ_b [M L⁻³] the soil bulk density, S [M M⁻¹] the concentration of the sorbed phase, v [L T⁻¹] the pore water velocity, D [L² T⁻¹] the hydrodynamic dispersion coefficient, $F(C, S)$ a function describing reactions of the substance in the solid and liquid phases (e.g. decay, kinetic sorption–desorption, precipitation–dissolution), t is time [T], and z the vertical coordinate [L].

As for Richard's equation, the CDE may be solved analytically under certain conditions, but it is most often solved in its numerical form. Main parameters for the CDE are pore water velocity and the hydrodynamic dispersion. Vanderborght et al. (2007) presented an interesting analysis of already published work where they calculated or extracted dispersivities from tracer experiments that they classified according to three varying factors; scale of experiment (soil core, column, field), flow rates

(from 1 to 10 cm day⁻¹), and travel lengths (length/depth of core or depth of soil). By inverse modelling using the CDE and breakthrough curves (BTC) the dispersivity was deduced as hydrodynamic dispersion divided by pore water velocity (assuming that molecular diffusion of the substance in bulk water can be neglected). The dispersivities ranged about three orders of magnitude (from 1 to 1000 cm) and were found to increase with increasing transport distance (depth of sample) and scale of the experiment. The activation of large inter-aggregate pores may explain the increase in dispersivity with increasing flow rate in fine-textured soils, a trend which was not observed in soils with a coarser texture Vanderborght et al. (2007).

Inter-aggregate soil water flow combined with intra-aggregate flow belongs to the definition of preferential soil water flow, i.e. a flow system with two possible flow rates. According to Kodešová et al. (2008) soil-porous systems are often bimodal or multimodal with a hierarchical composition of pores. Coppola (2009a) states that macro porous soils often exhibit a variety of small-scale heterogeneities such as cracks, inter-aggregate (or structural) pores, decayed root channels and other types of macropores and coarse micropores. Due to these local-scale heterogeneities preferential flow generally occurs, creating local-scale non-equilibrium conditions with regard to pressure head and solute concentrations among regions of faster and slower flow.

Preferential flow is not only a theoretical challenge but very important in reality, especially in fine textured soils as it increases the risk of contamination of drain and groundwater (Coppola et al., 2009b), and even in coarse sandy soils preferential flow may occur caused by fingering (Coppola et al., 2009a). An important condition along the flow path is that the organic matter content is lower in the lower soil horizons compared to the topsoil. Hence, in the upper horizons a higher buffer capacity for adsorption and higher biological activity exist - vital for the degradation of pollutants.

When preferential flow takes place in non-capillary macropores as bio-pores or soil cracks, Richard's equation is not applicable. Instead, the kinematic wave equation or the simple Hagen–Poiseuille equation have to be applied as fluxes are significantly accelerated compared to those in the micropores.

In addition to transport of dissolved pesticides, studies on macro-pore and particle-facilitated pesticide transport have been carried out in the last decade (e.g. Kjær et al., 2011b). Hence, for soils with preferential flow patterns, the following questions have been investigated: 1) Are particles (or colloids 0.2 µm to 2 µm) released and transported in these soils, 2) Possible mechanisms for pesticide sorption and transport facilitated by particles. Poulsen et al. (2006) found from studies on intact soil cores that transport parameters for bromide and colloids were highly variable across the field. Fitting a MIM (mobile-immobile water phase) model to BTC (break through curves) resulted in the estimation of immobile-mobile water parameters, advective velocities and mass transfer parameters for bromide and colloids. The colloid advective velocities v_{Br} and v_{coll} were different, v_{coll} being around three times higher than the velocity parameter for bromide. Characterisation of soil structure and macro-pore flow

is more important than the quantity of dispersible soil colloids in estimating leaching of colloids (Poulsen, 2006).

Studies have been carried out to assess the effects of soil tillage and different soil structure. Gjettermann et al. (2009) studied particle-facilitated pesticide (glyphosate and pendimethalin) transport in sandy loam soil monoliths. The monoliths were obtained from a field with two different treatments, recently ploughed and drilled (four monoliths), and the other minimally disturbed (five monoliths) but with some straw on top. After rewetting the monoliths were sprayed with normal doses of the herbicides glyphosate (four monoliths) and pendimethalin (five monoliths). At day 5, 8, and 12 the soils were irrigated with 30 mm at a rate of 15 mm per hour (quite high for Danish weather conditions, Kjær et al., 2011b). Effluent was sampled and half of the amount was sieved 1.5 min after sampling to assess the importance of the time varied concentration of particle bound pesticide. The main results were that after three irrigations the leached amount of glyphosate varied from 0.007 to 0.32% of total amount applied and for pendimethalin the leached amount varied from 0.12 to 0.43% of amount applied. A high fraction of leached particular bound glyphosate was found, around 62% \pm 10% of the total leached, but for pendimethalin quite lower, 5 to 13%. Changed soil structure (ploughing and drilling) had a marked influence; more soil particles were leached compared to the no tillage soil.

Pesticides bound to particles and transported towards surface water and groundwater may undergo desorption/adsorption changes ratio along the path. Desorption of glyphosate from leached particles (> 0.2 nm) or from particles removed from the monolith surface due to splash erosion was studied (Gjettermann et al., 2011) using monoliths and treatments from Gjettermann et al., (2009), but only the monoliths sprayed with glyphosate were used. Around 10-20% of particle-bound glyphosate desorbed after 20 min from leaching and splash-eroded particles shortly after leaching or immersion, respectively, indicating that the processes of desorption from the different sources of particles were similar.

The adsorption/desorption K_d coefficient and the D_{50} (degradation half life time) are important parameters when describing the fate of pesticides, c.f. Chapters 2 and 3. The K_d mechanism may be important in more than two ways. A high value generally means low transportability; however, if the soil - in addition to high sorption capacity - facilitates preferential flow e.g. in a macro-porous system and promotes particle-facilitated transport, the pesticide leaching may even exceed the pesticide flow obtained with a lower sorption value and transported via matrix flow. In reality K_d - normally obtained from lab studies with a given pesticide to a given soil - shows quite some variation between soils. Weber et al. (2004) correlated K_d to soil parameters; organic matter content, clay mineral content, and (for some pesticides) pH. They found correlations (R^2) in the range of 0.55-0.99. Cardeal et al. (2011) summarised the most important conditions influencing the transport of pesticide to surface and ground waters: they are pesticide and soil physical-chemical conditions, soil biological properties, and the capacity for degradation. Some important measurable parameters in addition to those discussed

include chemical solubility, vapour pressure at different temperatures, the partition coefficient of organic carbon with water (K_{oc}), and the octanol-water partition coefficient (K_{ow}).

4.2 Pesticide fate models

Pesticide fate models account for a variety of processes including soil water flow, solute transport, heat transport, pesticide sorption, transformation, and degradation, volatilization, crop uptake, and surface runoff. A particular modelling challenge is to predict pesticide transport at very low leaching levels relevant for pesticide registration issues (Köhne et al., 2009).

Köhne et al. (2009) provided an overview of pesticide transport models that account for preferential flow. Table 4.1 gives their review of models and their modelling concepts with regard to solute transport, solute transfer, sorption, and degradation.

From a screening of the best available models for simulating pesticide displacement in structured soils (Table 4.1), Köhne et al. (2009) found that MACRO, RZWQM (Malone et al., 2004), and the HYDRUS (1D-, 2D or 3D) model set were the superior models when taking into account their a) ease-of-use; b) complexity and flexibility; and c) 'up-to-date-ness' with continued model upgrades and support for users.

Sources of uncertainty in pesticide fate modelling comprise obvious factors such as uncertainty in the choice of conceptual model, primary input data for characterising the site, and the pesticides to be modelled. This also includes methods to account for measurement errors and for spatial and temporal variability of environmental variables. However, important sources of uncertainty are also related to 1) the ability of the model to actually describe experimental observations because the model does not include all relevant processes taking place and 2) Modeller subjectivity and unintended use of the model due to (linguistic) imprecision in the definition of model parameters (Dubus et al., 2003). Techniques to assess uncertainty in pesticide fate modelling such as the Monte Carlo analysis (Dubus et al., 2003, Soutter and Musy, 1999) generally assume implicitly that the major uncertainties are associated with model input parameters and that the structure of the model is sound and correct, such that an adequate parameterisation of the model is possible. The contribution of sources of uncertainty other than those related to model input parameters is unknown (Dubus et al., 2003).

In order to reduce the effect of model user subjectivity, sample simulations and/or a protocol with rules for model setup for different scales and settings should be included with all model codes (Köhne et al., 2009).

Inverse parameter estimation should ideally use all available data (not sequentially use water, tracer, and pesticide data). However, such a parameterization is complicated due to the non-linearity of flow processes in variably saturated media. As already pointed out, for assessment of pesticide properties, standard batch or incubation techniques are usually not representative of in-situ unsaturated matrix conditions, even if they (by volume) approximately represent the matrix (Köhne et al., 2009b).

In many field studies, pesticide degradation under field conditions was found to be initially faster than that predicted from laboratory incubation tests. The likely reason is that environmental conditions in the field (temperature, soil moisture, nutrient concentrations, and daylight) vary and differ from the constant lab conditions. The open and diverse field system causes various dissipation processes to be lumped into a 'pseudo-degradation'. For example, initial volatilization of the applied pesticide may be accompanied by other dissipation processes such as photodecomposition on soil/plant surfaces, degradation by adapted microorganisms (Krutz et al., 2010), leaching, absorption, and root uptake. Hence, in model applications it is difficult to properly distinguish between actual pesticide degradation in the soil and combinations of other dissipation processes taking place in the field (Köhne et al., 2009b).

Table 4.1. Characteristics of the most common 1D-models for preferential transport of pesticides (from Köhne et al., 2009b).

	RZWQM	MACRO	HYDRUS-1D ^a	CRACK-NP	SIMULAT	PLM
Documentation	Ahuja et al. (2000a,b), Malone et al. (2004a), Wauchope et al. (2004), Ma et al. (2007)	Larsbo and Jarvis (2003, 2005)	Šimůnek et al. (2005), Šimůnek and van Genuchten (2008)	Armstrong et al. (2000b)	Diekkrüger (1996)	Hall (1994), Nichols and Hall (1995)
Model concept (s)	DPM, DP-MIM	SPM, DPM	SPM, MIM, DPM, DP-MIM	MIM	DPM	DP-MIM
<i>Solute transport</i>						
a) Matrix	Convection, partial mixing	Convection–dispersion	Convection–dispersion	Immobile	Convection–dispersion	Immobile
b) PF domain	Convection, mixing (expon. depth decrease)	Convection	Convection–dispersion	Convection	Convection	Convection
<i>Solute transfer</i>						
a) PFdomain-matrix	Instant mixing with a boundary matrix layer	First-order advection–diffusion	First-order advection–diffusion	Advection (Philip)–diffusion (Fick)	Advection (Darcy)	Advection
b) Matrix-PFdomain	Instant mixing with a boundary matrix layer	Advection (routing), first-order diffusion	First-order advection–diffusion	Diffusion-like ^c , Peds-peds/peds-PFdomain	Advection(?) ^f	–
c) DP-MIM: mo-im	First-order diffusion	–	First-order diffusion	–	–	Diffusion-like ^c
<i>Sorption</i>						
a) Matrix	Linear, Freundlich, three-site (equilibrium, kinetic, bound or aged residues, pH-dependence)	Linear, Freundlich, two-site (equilibrium, kinetic), aging approximation	Linear, Freundlich, Langmuir, two-site (equilibrium, kinetic) ^b	Linear, Freundlich, (equilibrium)	Linear, Freundlich, Langmuir, (equilibrium, three sites)	Linear, (equilibrium), aging approximation in top 5 cm
b) PFdomain	No	Linear, Freundlich	Linear, Freundlich, Langmuir, two-site (equil.-kin.)	No	No	No/Yes (only in slow mobile water)
<i>Degradation</i>						
a) Matrix	First-order, function of T, θ (aerobic or anaerobic)	First-order, function of T, θ	First-order, function of T, θ ; Degradation on solid	First-order, function of T, θ	First-order or Michaelis Menten or (co)metabolic, function of T, θ	First-order, function of T, θ
b) PFdomain	No	first-order, function of T, θ	First-order, function of T, θ ; Degradation on solid	No	No	No
Heat flux	Yes	Yes	Yes	No	Yes	No
Root growth	Yes	Yes	Yes	Yes	Yes	Yes
Root uptake	Water, Solute	Water, Solute	Water, Solute	Water	No	No
Volatilization	Yes	(Yes)—lumped dissipation rate	Yes	No	No	No
Surface runoff	Yes	(Yes)	(Yes)	(Yes)	No	No
Solute in runoff	Yes	No	No	No	No	No
Management options	Crop rotations, tillage, fertilizer, manure, pestic. application mode	Tillage	No	No	No	No
Tile drainage	Yes	Yes	Yes	(Yes)	Yes	(Yes)
Inverse method	No	SUFI	Levenberg–Marquardt	No	No	No
GUI	Yes	Yes	Yes	No	No	No
Selected further features	Pesticide degradation on crop foliage and residue, crop growth and yield, organic matter and nutrient cycle, ion dissociation, chemical transfer to surface runoff, erosion	Swell-shrink dynamics, compaction, surface sealing, pesticide intersection canopy dissipation and washoff, uncertainty estimation, metabolites	Particle transport, CO ₂ transport, chemistry of carbonate system, major ion chemistry, metabolites	Swelling-shrinking, canopy interception		Time step is 1 day, space increment is 5 cm, no groundwater table

(ET—evapotranspiration, T—temperature, mo—mobile region, im—immobile region, PF—preferential flow, K_D —Sorption distribution coefficient, θ —soil moisture content, (Yes) means: is considered, but in a simplified way, SPM—single porosity model, MIM—mobile-immobile water model, DPM—dual-permeability model, DP-MIM—dual-permeability model with immobile water), GUI—Graphical User Interface.

^aSimilar features are included in HYDRUS-2D and HYDRUS (2D/3D).

^bMulti-site sorption concepts such as kinetic, irreversible, and attachment-detachment based approaches are included in a special HYDRUS-1D versions (e.g., Wehrhan et al., 2007).

^cIn publications, the equations used for process description were not indicated.

5. Water flow and transport of pesticide at field and catchments scales

This section reviews flow of water and fate of pesticides in agricultural soils at a larger scale (field and catchment). Special focus has been given to flow in structured soils. These soils may feature macroporous systems that often enable a fast flow path from soil surface where the pesticide is applied, to drainage water and upper ground water. Sampling good and enough data at various scales is expensive, but still needed to describe the natural variability, and to assess the best parameters needed by hydrological/chemical models. The concept of scaling will be discussed in section 5.1 and some recent results from studies in Denmark will be presented.

The review by Vereecken et al. (2011) showed how pesticide distribution coefficients, K_d (the equilibrium sorption parameter) or its organic carbon normalized K_{oc} may appear very different when they are assessed at different scales. Values for K_{oc} are typically derived from sorption isotherms obtained from batch experiments in lab. The experimental conditions differ considerably from larger-scale conditions so model simulation of the fate of pesticide may lead to results with only limited validity.

Several studies (Vereecken et al., 2011) have shown that pesticide transport is controlled by a combination of equilibrium and rate-limited sorption, but K_d continues to be determined from adsorption isotherms in batch experiments using standard protocols that can be easily implemented and run (e.g., OECD guidelines for testing chemicals, described herein; OECD, 2000, 2004). It seems that at least two types of sorption sites exist: (i) a site directly in equilibrium with the concentration in the liquid phase and (ii) a site showing non-equilibrium sorption (the parameter is affected by water flow). Assessing improved in situ sorption parameters may be achieved from inverse modelling where quality data is available in a field experiment containing BTC (Break True Curve) for a tracer and the pesticide of interest. For equilibrium situations the classical CDE (convection dispersion equation) may be used e.g., van Genuchten and Wierenga, (1976). For non-equilibrium situations two-site/two-region transport models may be used (Gamerding et al., 1990).

Spatial variability in hydraulic conductivity and important pesticide transport parameters appear horizontally and vertically at field scale. In a review, Janniche et al. (2011) deduced from former studies that spatial variability in sorption and degradation parameters had mainly been studied in the topsoil or the upper meter of agricultural soils. Janniche et al. (2011) studied the vertical variation of sorption and mineralization of three herbicides based on soil samples from 4.5 m to 26.4 m depth in a field within an agricultural catchment in Brévilles, France. The deepest layer was within the saturated zone. All three herbicides mecoprop (MCP), isoproturon, and acetochlor showed strong sorption around 5 m below soil surface, and nearly none in the 7 m and 25 m layers.

Spatial variability in parameters and flow patterns for water and pesticides are pronounced in structured soils. Further, these soils are most often drained to allow farmers' field operations in spring and autumn, and the drainage systems add to the variability in flow patterns. Since 1976 when the concept of preferential flow was introduced (Coppola et al., 2008a) scientists have been exploring flow phenomena in structured soils at field and catchment scale (e.g. Coppola et al., 2009b; Köhne et al., 2009a,b).

The increased number of observations of pesticides in ground water in Denmark promoted discussions on establishment of a pesticide monitoring programme. In 1999, the Danish Pesticide Leaching Assessment Programme (PLAP) was launched (e.g. Kjær et al., 2011a), and in parallel research activities with focus on the fate of pesticides was markedly increased.

During the last decade Danish research groups have studied pesticide transport in structured drained soils and the risk of contamination of drain water and ground water (Kjær et al., 2005a; Rosenbom et al., 2008; Rosenbom et al., 2009a; Rosenbom et al., 2009b; Juhler et al., 2010; Nielsen et al., 2010; Gjettermann et al., 2011; Iversen et al., 2011; Kjær et al., 2011b; Nielsen et al., 2011).

Kjær et al. (2005a) analysed samples of soil water collected with suction cells, drainage water, and upper ground water, at three PLAP sites. The herbicide glyphosate and its degradation product AMPA, did not appear in ground water, but drainage water had average concentrations exceeding $0.1 \mu\text{g L}^{-1}$. The main flow path was thought to be through macro pores; however this hypothesis was not tested. AMPA was found more than 1.5 years after the application.

To study the mechanism controlling preferential flow two tracers were applied in a field experiment to an irrigated variably saturated clayey till, at Gjorslev, Denmark, (Rosenbom et al., 2008). In a 2D excavation reaching to the depth of 2.8 m, the flow of two different fluorescent tracers Acid Yellow 7 (AY7) and Sulforhodamine B (SB) were analyzed. The main conclusion was that both tracers during dry and wet initial climate-conditions primarily migrated rapidly through one-dimensional biopores to a depth of app. 1.2 meters and further into a three dimensional network of tectonic fractures. Dead-end biopores were only activated for tracer-migration at dry initial climate-conditions.

Rosenbom et al. (2009a) calibrated and "validated" the three dimensional model Hydro-GeoSphere based on data from the experimental site at Gjorslev (Rosenbom et al., 2008). The model reproduced reasonably well the observed preferential migration of AY7 and SB through the fractured till, although it did not capture the exact depth of migration and the negligible impact of the dead-end biopores in a near-saturated matrix. A sensitivity analysis suggested that the system contains fast flow mechanisms and dynamic surface coating in the biopores, and the presence of a plough pan in the till.

At three PLAP field sites, Jyndevad (coarse sandy soil), Estrup, and Silstrup (clayey till soils) Juhler et al. (2010) studied the dissipation of the growth regulating pesticide chlormequat (Cq). Batch studies (repacked sieved soils) were carried out in the lab to assess adsorption and desorption characteristics at different pesticide concentrations. DT50 was found to be 21 to 61 days and $K_{d,ads}$ (adsorption) and

$K_{d,des}$ (desorption) coefficients were described with Freundlich isotherms. K_d distribution coefficients were found to be 2 to 566 $\text{cm}^3 \text{g}^{-1}$, lowest in the sandy soil. The main results were that Cq was strongly adsorbed to soils and desorption was low, less than <10%w. In water samples, out of a total of 282 (119 at Estrup, 122 at Silstrup and 41 at Jyndevad), the pesticide was found in only two at concentrations < 0.02 μg . The samples from Estrup and Silstrup were drainage water samples. The results indicated that the leaching risk posed to the aquatic environment by chlormequat is negligible.

Nielsen et al. (2010) studied the distribution of biopores (>1mm) in a sandy loam till with drainage pipes at 1.2 m depth, 16 m apart. Two excavation areas, A and B, were established in the field after irrigation of a well-defined plot with 50 mm of water with a concentration of 2.2 g L^{-1} of Brilliant Blue. The areas were 10 m apart and at one end crossed the drainage pipe (the length direction of the areas was perpendicular to direction of pipes). Eight terraces distributed at depths 15 to 175 cm were established so in both areas a total of 14 m^2 was available for description of biopores, fractures and voids. The number of biopores was of the same order of magnitude at study sites inside and outside the drainage trench, varying from 0-1114 m^{-2} . Stained biopores (0-833 m^{-2}) in the horizontal direction were unevenly distributed and not affected by distance to the drainage pipe (0-5.5m). However, in the vertical direction the number of dead pores decreased at 50-75 cm depth, but active pores (< 100 m^{-2}) were found at the depth 150 cm, where they were connected to fractures. The filled in soil above the drain pipe showed a similar distribution of biopores with depth as the soil outside the filling (0-5.5m), however this heterogeneous mixture of A and B horizon soil above the drain pipe had caused several preferential flow paths, such as flow at interfaces between the different soil types and flow in small root channels along the border of the till and filling. Another observation was that the drain pipes showed a network of stained biopores in addition to the macro-pores related to the introduction of the drainage system. This continuum of pores connecting the surface with the drain pipe provides a potential pathway for the direct transport of water and surface-applied chemicals into the drain pipe. This transport may happen at high precipitation intensities when the ground water level is well below the drain pipe and it may be that this preferential flow system in initially dry soil conditions supplement the preferential flow in fractures starting at around 1.5 m depth in more wet soil conditions.

Nielsen et al. (2011) studied preferential water flow and transport at the same site as Nielsen et al. (2010) but one year later. Fluorescent melamin-resin microspheres (MS) were used to represent colloids. The MS were sized $0.98 \pm 0.06 \mu\text{m}$ and produced with a covering of a dye, Sulforhodamine B monosodium salt. Irrigation water containing Brilliant Blue (BB), Bromide (Br), and MS was added to a well-defined plot over a 4-h period. BB is a reactive tracer, opposite Br, and shows a non-linear sorption when concentrations are less than 10 g L^{-1} . The tracer study of Nielsen et al. (2011) revealed that the retention and the distribution patterns of Brilliant Blue (BB), bromide (Br), and fluorescent microspheres (MS) differed between and along macropores. An interpretation of the distribution patterns along macropores indicated that the interaction and mobility of water between the macropore and matrix was important. Moreover, it was recognized that the concentration of tracer along the

biopore walls examined in the drain trench did not necessarily reflect the concentration of substances transported through the biopores. Distinct differences in transport and retention between the till and the drain trench was observed when comparing the bromide and microspheres distributions quantitatively. It was notable that the proportion of samples with measurable concentrations of MS and Br in the drain trench was significantly higher than the proportion of samples from the till at the depth of the drain pipe (1–1.25 m). This implies that substances can be accumulated along the drain pipe during heavy precipitation events. Hence, these findings suggest that it would be valuable to assess the remobilization potential of retained substances along the drain pipes in future studies.

In relation to the samples from the drain trench, it was found that solutes such as Br and weakly to moderately retarded substances represented by the dye BB can enter the drain pipe and thereby surface water in an undiluted state, while solutes represented by MS colloids entering the drain pipe may be filtered.

Leaching of glyphosate and pendimethalin was measured in drainage water at the PLAP site in Estrup, a tile-drained loamy soil with a geological complex structure (Kjær et al., 2011b). They found concentrations of pesticides dissolved in soil water above $0.1\mu\text{g L}^{-1}$ for more than seven days. At three rain events intensive sampling of particle-facilitated (particles $> 24\mu\text{m}$) and dissolved pesticides showed similar leaching patterns even if glyphosate sorbs strongly to mainly minerals, and pendimethalin sorbs mainly to organic sorption sites. Particle-facilitated transport of pesticides accounted for only a small proportion of observed leaching, 13-16% for glyphosate and 16-31% for pendimethalin. Particle-bound pesticide was transported solely by vertical transport in macropores and rapid lateral transport occurring near the drain line whereas dissolved pesticides were transported laterally over larger distances through the saturated zone via discontinuities in the soil.

Flow in sandy soils is less complex as water flows mainly through the soil matrix. However, still these soils are prone to leach agrochemicals from the root zone and towards surface and groundwater. Kjær et al. (2005b) studied the transport of metribuzin and its primary degradation products (metabolites); desaminometribuzin (DA), desaminodiketometribuzin (DADK) and diketometribuzin (DK) in a sandy soil, the PLAP site in Tylstrup. Metribuzin was applied in May and June 1999 and as such leaching of Metribuzin was not expected as its dissipation rate (DT50) is reported to be 11 to 46 days, however having low absorption capacity. Soil water samples were collected over a four year period from the unsaturated and saturated zone. Three months after the Metribuzin application quite high concentrations $> 0.1\mu\text{g L}^{-1}$ of metabolites DADK and DK were found in water samples from one and two meter depths. Based on the four year study period, Kjær et al. (2005b) concluded that metribuzin and DA showed a negligible leaching, but DK and DADK leached from the root zone (1 meter below ground surface) in average concentrations well above the EU limit for drinking water ($0.1\mu\text{g L}^{-1}$). Both metabolites appeared to be relatively stable and persisted in soil water and groundwater several years after application. Except for three of the groundwater samples, the DADK concentration never exceeded the EU limit value. In contrast, the annual concentration of DK exceeded $0.1\mu\text{g L}^{-1}$ at 90% of

the screens analysed. The findings suggested that as the degradation products of metribuzin can leach through sandy soil in high concentrations, they could potentially contaminate groundwater.

Rosenbom et al. (2009b) tested the MACRO-model predicting long-term leaching of the herbicide metribuzin and its degradation product diketometribuzin in a sandy field Tylstrup, DK. The MACRO-model is one of the models recommended for use at European level for assessing fate of pesticides in agricultural fields and risk of transport to surface and ground waters (FOCUS, 2000). From the present modelling it was concluded that MACRO in its standard setup was unable to accurately simulate the long-term fate of metribuzin and diketometribuzin; the concentrations in the soil were underestimated by many orders of magnitude. However, if MACRO was changed in its formulation of the degradation process, meaning the kinetic degradation of pesticides changed to a two-site approach, fairly good agreement was obtained.

5.1 Scaling from field to catchment

Scaling related to hydrology is a very important issue, still not solved, and hence subject to ongoing research. Quite some effort has been allocated to modelling at catchment scale i.e. leaching of water, nutrients, and other agrochemicals to ground and surface waters. To describe the flow in the unsaturated and saturated domain, important hydro-chemical characteristics must be included in the models.

To better understand the dynamics within the catchment, we need to get more detailed and accurate description behaviour of system parameters both in time and space. New model elements need to be developed and existing ones must be improved as they have often been included in a “lumped” fashion.

Refsgaard (2007) gave an overview of catchment modelling and results obtained within the last three decades. The major themes discussed were: a) new conceptual understanding and code, b) model validation, c) scaling, d) uncertainty assessment, and e) modelling protocols and guidelines for quality assurance in the modelling concept.

In the present study we summarise from Refsgaard (2007) results obtained within the topic scaling and distributed physically-based modelling. In a distributed model spatial variability is accounted for by dividing the catchment into several smaller elements. Hence, in scaling theory two different approaches can be distinguished:

1. *Upscaling* means that process equations and the associated parameters that basically constitute the model in principle are modified or substituted when moving from the smaller to the larger scale
2. *Aggregation* means that the process equations are still applied at the smaller scale (where they were derived) and large-scale results are obtained by aggregating the small-scale results up to the larger scale.

Future studies of reactive transport modelling, e.g. nitrogen and pesticide transport from field to surface and ground waters need to represent heterogeneity much more explicitly.

Catchment distributed physically based-modelling implies that the vadose zone of the catchment is subdivided into smaller representative areas, vertical units of soils and crops, which supply parameters to a physically based generic one-dimensional model for crop production. These models are then coupled simple to a three-dimensional groundwater model, even if in several cases two/three-dimensional modelling of the unsaturated zone is needed. 'Simple coupled' means that the one-dimensional calculations of leachate (water and agrochemicals) in the unsaturated zone act as the upper boundary for the groundwater model. The hydro-chemical parameterisation of the unsaturated zone is normally based on measurements, or for some parameters based on pedo-transfer functions. Here the modellers often deal with too few point measurements and a high spatial variability, but still they need to average the data to their best representation of the domain of interest. Normally such a modelling complex needs calibration of single processes, modules, or the whole system, where especially measurement of ground water heads and measurements of stream flow are used for calibration.

Hansen et al. (2011) further developed the Daisy model to include two-dimensional transport of water and agrochemicals in the 1-2 m depths in a soil including drain systems. A biopore model was included that can handle different architecture of pores and the flow of water and solutes. A good parameterisation of biopores in the two-dimensional unsaturated domain is rather important as old worm channels may act as a direct link from the soil surface to the drain. Hansen et al. (2011) included modules for colloid transport and colloid facilitated transport of pesticides. The enhanced Daisy was tested at three sites, in Tåstrup especially with regard to colloid transport, and at Estrup and Silstrup, especially the pesticide data. The model needed calibration at all three sites and for Estrup and Silstrup a surface flow model needed to be included. Test results showed that the dynamics of pesticide leaching were well described at Tåstrup, and some part of the pesticide leaching was well described at Estrup.

To model transport of water and agro-chemicals at catchment scale the Daisy model was fully coupled with MIKE SHE (Graham and Butts, 2006) facilitated through the Open MI modelling interface (Gregersen et al., 2007). The coupling implies that the upper boundary for MIKE SHE is the lower boundary for Daisy. Data from the Lillebæk catchment was used to test the complete model system (Daisy2D coupled to MIKE SHE), i.e. water flow and transport of pesticides from field to various recipients (drains, stream and ground water).

The conclusions of the tests runs and calibrations of the two-dimensional Daisy-model and the coupled model system Daisy2D-MIKE SHE were presented by Hansen et al. (2011) on p.130-133. We cite a few statements with focus on the coupled model system. Hansen et al. (2011) states: "Even if the coupled model does not accurately reproduce field data in the Lillebæk catchment, the new first results

show that the new concept for up scaling is very useful at catchment scale, and the new processes included in Daisy at field scale have a marked influence on pesticide transport and concentrations at catchment scale.”

6. Effects of climate and management, and their interactions on pesticide losses

When pesticides are applied at field scale, there will be some immediate losses (spray drift, volatilization and photochemical degradation). The climatic conditions impact on the amount of spray that will be deposited downwards. Fritz and Hoffmann (2008) investigated atmospheric effects on the fate of agricultural sprays and found that no single meteorological factor dominated the downwind transport of aerially applied sprays. Generally, lower relative humidity decreased the amount of downwind deposition due to evaporative effects. Increasing wind speeds decreased deposition and increased the amount of mass that could not be accounted for in the experiment.

Pesticide losses by leaching and drainage show considerable temporal variability owing to random weather patterns. The timing of rainfall and extreme events in relation to application date were of prime importance (Nolan et al., 2008). Model-predicted cumulative pesticide loss generally increased with increasing rainfall of variable duration, decreasing temperature and increasing pesticide persistence, for both leaching and drainage scenarios (Nolan et al., 2008). Weather interacts strongly with soil type such that short-term climatic variables are generally more influential in soils with high clay content. However, the influence of these variables and the timing of extreme events in relation to pesticide application were greater for drainage scenarios than for leaching scenarios (Nolan et al., 2008). The results of Nolan et al. (2008) reflect the rapid transport of pesticides to drains via macropores in soils with high clay content.

Larsbo et al. (2009) investigated pesticide leaching from Swedish soils under conventional tillage and reduced tillage. They found that reduced tillage has the potential to reduce pesticide leaching but that any reduction may be counter-balanced by enhanced preferential flow for soils where reduced tillage results in improved macropore connectivity.

At the landscape scale, a catchment's topography (governing the flow paths of surface water) and the position of landscape elements such as hedges, riparian buffer strips, or grassed waterways influence if and how much pesticide lost from a given field in the catchment finally reach a surface water body. The effectiveness of grassed buffer strips located at the lower edges of fields has been demonstrated in general. However, this effectiveness is very variable, and the variability cannot be explained by strip width alone. Riparian buffer strips are most probably less effective than edge-of-field buffer strips in reducing pesticide runoff and erosion inputs into surface waters (Reichenberger et al., 2007).

The loss of pendimethalin, a selective herbicide, was determined in runoff water from loamy soil plots of various surface slopes cultivated with tobacco, over a period of 193 days. Conditions were selected to simulate agricultural practices employed in the Mediterranean region. The surface slopes of plots were 0%, 2.5%, 5%, 7.5%, and 10% and cultivated and uncultivated (control) areas were monitored. The cumulative losses of pendimethalin in surface runoff, as percentage of the initial applied active

ingredient, were 0.067% for tilled and 0.098% for untilled soil of 10% slope, while for the plots of 0% slope they were ten times lower, 0.006% and 0.009% respectively. The maximum concentrations in runoff water reached $16 \mu\text{g L}^{-1}$ and were detected after the second runoff event. The dissipation in top soil was studied for a period of 129 days. The half-lives that were calculated using first order kinetics ranged from 23 to 27.2 days in non-cropped soil and from 22.3 to 26.2 in tobacco plot (Triantafyllidis et al., 2009).

Locke et al. (2008) found that conservation tillage and field slope had quite an effect on surface runoff on water and of pesticides after a heavy rain fall event (25 mm in 20 min). Total alachlor loss was greater in conventional tillage plots (4.5% vs. 2.3% in no-tillage), primarily as a function of total runoff loss, with more than one-third of total alachlor loss from conventional tillage plots occurring in the first runoff fractions. The other herbicide chlorimuron has a more polar characteristic and was likely removed from surface plant residues by rainfall and lost in runoff with little soil interaction. Thus, chlorimuron wash off from the residue likely contributed the most to the difference between no-tillage and conventional tillage in runoff.

7. Regional scale modelling

7.1 Soil based initiatives

The Danish research project KUPA (www.kupa.dk), which was a collaboration project between Geological Survey of Denmark and Greenland (GEUS) and Institute of Agroecology, Aarhus University, aimed to develop a concept on how to identify pesticide vulnerable areas. The work was separated in two phases, first a sandy soil concept (Nygaard, 2004), and later a clay soil concept (Gravesen and Rosenberg, 2009).

Based on the studies of the sandy soils the following conclusions were drawn (Nygaard, 2004): It is possible to point out the sandy soil locations that are particularly sensitive to pesticide leaching, based on the soil hydraulic conductivities and pesticide sorption characteristics, since:

1. There is a relationship between simulated leaching of pesticides and several ordinary soil characteristics that are relatively easy to assess.
2. Pesticides - with few exceptions – belong to a group where the tendency to leach has the same overall dependency of soil characteristics, meaning that in general they will leach from the same area, and soil mapping can be based on common characteristics.

The work included: 1. Literature review on pesticide leaching from sandy soil, 2. Establishment of new data based on field studies, test sampling and laboratory experiments 3. Simulation of leaching with MACRO3.4 model, 4. Assessment of relationships between soil and model parameters, and 5. Assessment of relationships between soil parameters and pesticide leaching.

In the KUPA clay soil concept (Gravesen and Rosenberg, 2009) the work was focused on:

1. The possibility to predict areas with clay soils vulnerable to pesticide leaching down to 2 m depth.
2. For these areas predict the sensitivity for leaching and transport towards the upper ground water.

The KUPA project concluded that it is possible to describe the sensitivity of clay soils for leaching pesticides to the bottom of the root zone. However, it was not possible to develop a method for areas with clay soils, which could describe the sensitivity of the transport of pesticides just below the root zone towards the groundwater. Hence, the KUPA project could not present a complete concept that describes areas with clay soils vulnerable to leaching of pesticides to the ground water.

More studies could be identified based on the KUPA-results, especially on the need for further data to characterize the soils below the root zone, and the possibility of GIS maps being helpful when pointing out soil, landscape or regional areas with high risk for pesticide leaching to the ground water. In many clay soils, internal structures and biological activities have created preferential pathways (macropores and biopores) that are important transport routes for pesticides and other contaminants.

At present, macropore flow cannot be satisfactorily predicted (Iversen et al., 2011), but with the current use of agrochemicals especially by farmers there is a need for models or information tools to point out risk areas for loss. Iversen et al. (2011) developed pedo-transfer functions for saturated and near-saturated hydraulic conductivity for soils across Denmark. Using these distributed data combined with a recently developed raster-based property map, a new map for Denmark could be constructed to point out areas where macropore flow is likely and hence where there is risk for leaching contaminants from the root zone.

7.2 Overview of Danish pesticides use

'Pesticides' covers a variety of agents for protecting crop growth from weeds, diseases and insects. In Denmark, herbicides constitute the majority (c. 65-80 %) in terms of weight of agents and weight of active ingredients (Miljøstyrelsen, 2011). Fungicides represent 15-20 % of pesticide use while plant growth regulators, algicides, insecticides, etc. represent smaller fractions of total pesticide use. In 2010, the total number of different active agents was 78, of which 43 were herbicides, 21 were fungicides and 8 were insecticides (Miljøstyrelsen, 2011). Glyphosate contributed with about 50% of total herbicide purchase in 2010.

7.3 Pesticide treatment frequency index (TFI)

A measure for quantifying and comparing pesticide use across years and regions is the pesticide Treatment Frequency Index (TFI). It was introduced in 1986 and is the theoretical number of pesticide treatments per hectare, calculated by dividing amount of pesticides sold for agriculture by the total area treated and the standard approved dosages of each pesticide. The overall aim of the Danish Pesticide Action plan has been to reduce the use of pesticides as much as possible without causing significant economic losses. During 1981-1985, the average TFI was 2.67, the 2008-2010 average TFI was 2.8, (Figure 7.1) and the current political target for reducing pesticide use is reducing the average TFI to 1.9 (<http://www.skm.dk/public/dokumenter/lovstof/2012/pesticid/lovforslag.pdf>). The TFI quantifies average pesticide use in terms of mass of active ingredients, but is not able to account for differences in pesticide effects on the environment or toxic effects of a given pesticide on organisms (Sattler et al., 2007). Several attempts to develop a more precise method of determining the environmental load caused by pesticides than the TFI have not been successful (Jørgensen and Kudsk, 2006). A recent report (Miljøministeriet 2012) suggested calculation principles for a Pesticide Environmental Stress Indicator (PBI) that was recently included as an administrative tool for allocating environmental taxes to different pesticides as introduced in a national tax bill on pesticides (http://www.mim.dk/Nyheder/20120126_Pesticidafgift.htm).

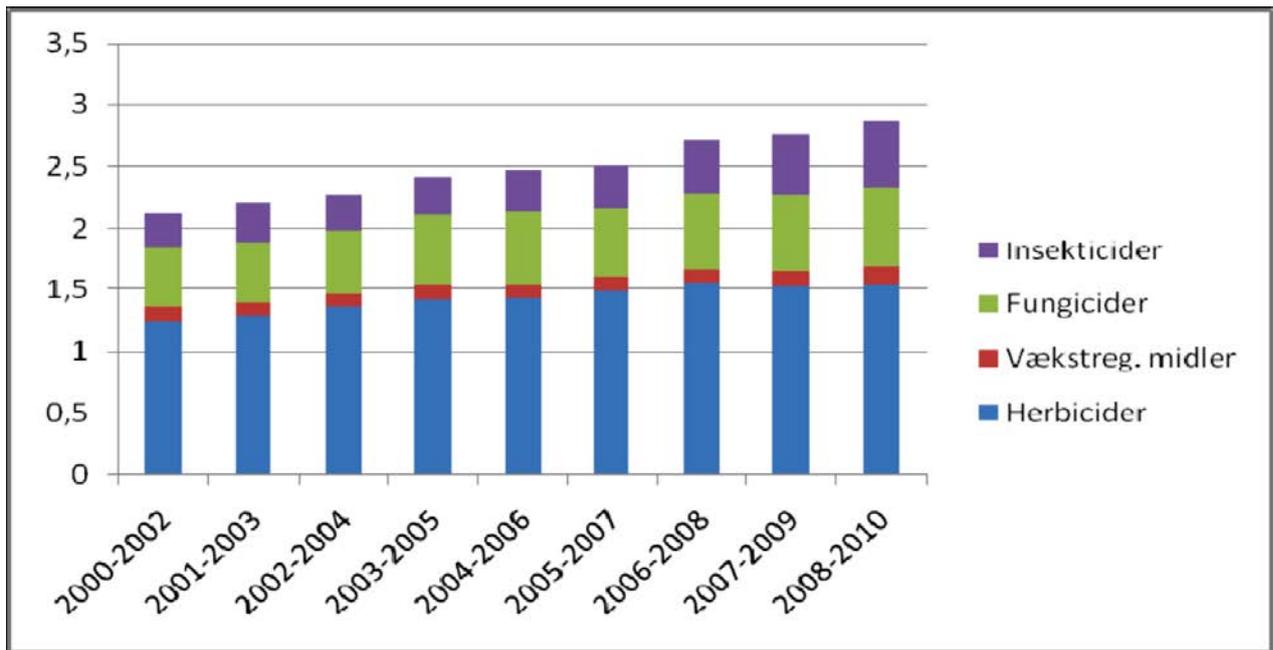


Figure 7.1. Treatment frequency index (TFI) in Denmark, three-year means between 2000 and 2010. Contributions to TFI from Insecticides (purple), Fungicides (green), Plant growth regulators (red) and herbicides (blue) are given. Figure from Miljøstyrelsen (2011).

7.4 Analysis and mapping of pesticide use at a regional scale

To get a regional perspective on the risk for leaching of different pesticides from agricultural land, a number of information sources are found to be crucial. As already mentioned, different landscape and soil types have different hydraulic transport mechanisms (matrix and macro pore flow), and these mechanisms are important in relation to the risk of transport of pesticide and their metabolites to deeper soil layers. Another important factor when dealing with the regional scale perspective is the actual use (mean dose sprayed at the fields) of the different pesticides. When the application in a region is very limited, the risk of losses of the particular pesticide is also very low, and similarly, wide application leads to high risk of losses. Some pesticides are crop specific and therefore only used in certain crop rotations. Special crops as vegetables, potatoes and beets are grown intensively in certain regions in Denmark and so the risk for leaching of these pesticides is higher in these regions.

To provide a regional perspective on mean pesticide use we developed a method to estimate the actual mean pesticide use at regional scale. Based on this method, maps of mean applied doses of the different herbicides used in the years 2007-2009 in Denmark were calculated.

7.4.1 Method

A method was developed on how to calculate the mean dose of a pesticide, or actually of 43 herbicides, their applied amounts and their use in the period 2007, 2008 and 2009. Based on herbicide doses for different crops, total annual herbicide use at national level, and actual land use (cropping patterns) obtained at the field block scale (size from 1-100 hectare, average 10 ha), average herbicides doses were simulated and aggregated at 10 km square grid level for Denmark. Based on the 10 km grid results, we used the interpolation method *kriging* to calculate maps of national herbicide use. The average doses were calculated as averages for the agricultural area only. The agricultural area included the conventional and organic production areas although the latter areas are not treated with herbicides. The variation in non-agricultural areas (e.g. natural areas, roads, towns, forest etc.) between the grid cells did not affect the mean dose results. The results of the analysis are presented in figures 7.1 to 7.8. Not all maps represent average results for all three years (2007 to 2009). If the herbicide was only used for one or two years, the results are based on these years.

In the analysis we did not take into account the effects of different cropping systems (e.g. arable cropping systems versus green fodder cropping systems) or the needs for specialised weed control. It has not been within the scope of this project to describe this influence of cropping sequences on the use of the different herbicides. The herbicides are used only in relation to crop type. As the results are aggregated to 10 km grid scale, many different cropping systems are represented in the mean result. It is assumed that the error related to special herbicide needs in cropping systems is minimized by aggregating the results to the 10 km grid scale. The mean agricultural area of the 10 km grid cells is

app. 4930 ha, so often more than 20 farms are represented in the mean result. The results cannot be used at a smaller scale (field or farm scale) as the input data of the analysis and the methodology are not sufficiently accurate to apply at small scale.

Land use data

Data from national databases (General Landbrugs Register (GLR), described in Børgesen et al., 2009) on land use for the arable land for the years 2007, 2008, and 2009 were used in the calculations. The different GLR-codes were classified into 11 classes as used in the national statistics on pesticide use (Miljøstyrelsen, 2008; Miljøstyrelsen, 2009; Miljøstyrelsen, 2010). The classes are: 1: Winter cereals, 2: Spring cereals, 3: Winter oil seed rape, 4: Spring oil seed rape, 5: Other seeds (mainly different varieties of grass seeds), 6: Potatoes, 7: Beets, 8: Peas, 9: Maize, 10: Vegetables, 11: Grass and clover. We only considered grass- and clover fields in rotation in the class Grass and Clover. Permanent grass was not assumed to be sprayed with any herbicides.

Herbicide dose

Herbicide doses called “normal dose” used in the analysis were based on the “new method” described in the national statistics reports (Miljøstyrelsen, 2008; Miljøstyrelsen, 2009; Miljøstyrelsen 2010). The doses are specific for the 11 categories of crops. Doses are quantified as gram of Pesticide Active Ingredient (PAI).

Simulation at 10 km grid scale

Mean doses were simulated using the fertilization module of the SKEP/DAISY simulation system (Børgesen et al. 2009). The system was upgraded with a module that simulates the use of herbicides at field scale level, based on GLR land use data, and data on recommended crop specific herbicide doses, and the total pesticide use at national level. As the model system can calculate N fertilization at farm level, this will also be an option when herbicide use data are available at farm scale level.

The first step in the calculation was to obtain the total potential use of each herbicide for each of the three years using the recommended doses for all crops at national level. In the second step the doses were calibrated to the actual mean dose level, by calculating an annual herbicide- specific calibration factor. This was done to calibrate the mean dose so that the actual total use balanced the use at the national level.

Creation of maps using GIS

All field block results were aggregated to 10 km grid scale level. The total herbicide use within each grid was converted to a mean dose by dividing the total calibrated herbicide use with the total agricultural area within the 10 km grid cell. The mean doses were then used in an interpolation procedure using the Spatial Analyst kriging procedure within the ArcGis software version 10.1. In the analysis we used 12 km as max distance between the interpolation points, meaning that the effect between areas without grid cells was not included.

7.4.2 Results

The results of the analysis are presented in Fig. 7.1 to 7.8. In each figure four to six maps are presented. Each map presents mean doses of one type of herbicide used within the period 2007-2009. To make the figures (results) as logical as possible we used the same legend for all maps within the same figure. Note that the legends change between figures. Thereby the results cannot be compared on absolute values between the figures, but only on a relative basis.

Fig. 7.1 shows results for the herbicides with max dose ranging from 0.1 to 0.29 g PAI ha⁻¹. Fig 7.1a represents mean dose of triasulfuron, being used only in 2009, with a total use of 17 kg PAI and a normal dose of 4 gram PAI ha⁻¹. This herbicide is used for spring cereals at a very low total use, resulting in low average dose of 0.006 g PAI ha⁻¹. As spring cereals are grown on all soil types this herbicide has a very even spatial distribution.

Fig. 7.1b represents mean dose of dicamba, which was used only in 2009. The mean use was 348 kg PAI year⁻¹ and the normal dose is 200 g PAI ha⁻¹. The herbicide is used for spring cereals and winter cereals gives a very low average dose, with a max. dose of 0.23 g ha⁻¹. As spring cereals and winter cereals are grown on all soil types this herbicide has a relatively even distribution. The mean dose for the agricultural area is 0.12 g PAI ha⁻¹.

Fig. 7.1c and 7.1e represent mean dose of clodinafop-propargyl and mesosulfuron, respectively. Both herbicides have been used in all three years with a total mean use of 252 kg PAI and 382 kg PAI respectively. The normal dose for clodinafop-propargyl and mesosulfuron, respectively, are 40 and 11g PAI ha⁻¹, respectively. These herbicides are used for winter wheat and generally applied in low doses (mean 0.09 g PAI ha⁻¹ and 0.14 g PAI ha⁻¹ respectively) with the highest dose up to 0.20 g PAI ha⁻¹ and 0.26 g PAI ha⁻¹. As winter cereals are grown on more loamy soil types these herbicides have higher dose in regions dominated by these soil types. Loamy soils dominate in the north western and eastern part of Jutland and on the islands Fyn and Zealand and on the southern islands.

Fig 7.1d represents mean dose of thifensulfuron-methyl which has been used in all three years with a total mean use of 379 kg PAI year⁻¹. This herbicide is used in spring and winter cereals, maize and grass/clover. Normal dose is 11.25 g PAI ha⁻¹ for winter cereals, 7.5 g PAI ha⁻¹ for spring cereals and maize and 18.75 g PAI ha⁻¹ for grass and clover. Average dose is 0.18 g PAI ha⁻¹ and the highest dose goes up to 0.18 g ha⁻¹. The lowest dose is found in central Jutland due to potato production and in the region south of Zealand where sugar beet production reduces the share of fields grown with cereals and green fodder crops.

Fig. 7.1f represents mean dose of sulfosulfuron that was used all years with a total mean use of 528 kg PAI year⁻¹ giving an average dose of 0.19 g PAI ha⁻¹. This herbicide is used in wheat with a recommended dose of 17.5 g PAI ha⁻¹. As cereals are the dominating crops in Denmark the distribution generally follows the areas outside the dairy cattle areas in the south/western and north central part of Jutland.

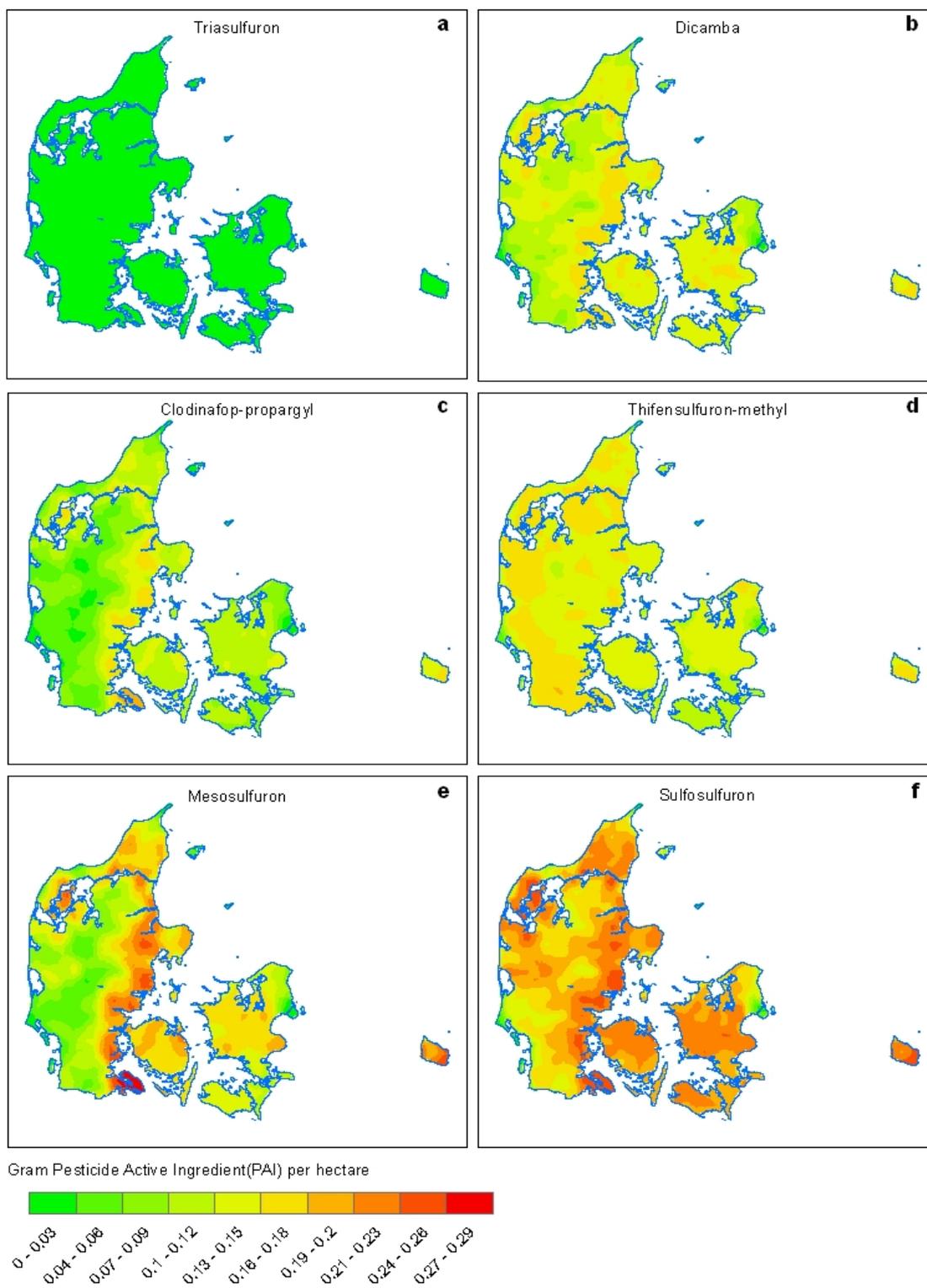


Fig. 7.1. Calculated mean doses of six herbicides.

Fig. 7.2 shows the results for the herbicides with second lowest max dose (0.3-0.81 g PAI ha⁻¹).

Fig. 7.2a, 7.2b, and 7.2e represent mean dose of florasulam, metsulfuron-methyl and tribenuron-methyl, respectively. These herbicides have been used in all years with a total use of 575, 674 and 1540 kg PAI year⁻¹ respectively. These pesticides are used in spring and winter cereals and in the category “other seeds” that primarily includes grass for seed production. Normal dose of florasulam is 5 g PAI ha⁻¹ for cereals and 7.5 g PAI ha⁻¹ for other seeds. Normal dose of metsulfuron-methyl is 6 g PAI ha⁻¹ for winter cereals and 4 g PAI ha⁻¹ for spring cereals and other seeds. Normal dose of tribenuron-methyl is 7.5 g PAI ha⁻¹ for the three crop types. The mean doses for florasulam, metsulfuron-methyl and tribenuron-methyl are 0.21 g PAI ha⁻¹, 0.25 g PAI ha⁻¹ and 0.56, respectively. These herbicides are used in winter and spring cereals and other seed which give a relatively even spatial distribution. Although it can be seen that the south western part (sandy soils) and north central part of Jutland with a high dairy production (high share of green fodder) have a lower dose compared with the rest of the country.

Fig. 7.2c represents mean dose of picolinafen and has been used in 2007 and 2008 with a total mean use of 524 kg PAI year⁻¹. The normal dose is 10 g PAI ha⁻¹. The mean dose is 0.19 g PAI ha⁻¹. This herbicide is used only for winter cereals and gives generally low doses with highest dose up to 0.46 g PAI ha⁻¹. As winter cereals are grown mainly on loamy soil types this herbicide has the dominating distribution on these soil types found on the eastern part of Jutland.

Fig. 7.2d represents mean dose of tepraloxydim and has been used all years with a total mean use of 254 kg PAI year⁻¹. This herbicide is used in potatoes, beets, peas and vegetables with a normal dose of 100g PAI ha⁻¹ for all crop types. For Denmark as a total the mean dose is very low (0.09 g PAI ha⁻¹) although there are areas with local higher doses. Especially the central part of Jutland near Karup, where there is a high production of potatoes, shows high mean doses. The same goes for Samsø (island north of Funen) with a high share of vegetables (dose up to 0.71 g PAI ha⁻¹) and for Lolland and Falster (South of Zealand) with a high share of sugar beets.

Fig. 7.2f represents mean dose of flupyr-sulfuron-methyl that was used in all three years with a total mean dose 363 kg PAI year⁻¹. This herbicide is used for winter cereals and shows generally low doses with the highest up to 0.30 g PAI ha⁻¹. The normal dose is 10 gram PAI ha⁻¹ and the mean for the country is 0.13 g PAI ha⁻¹. As winter cereals are primarily grown on more loamy soil types this herbicide has higher doses in regions where these soil types are dominating.

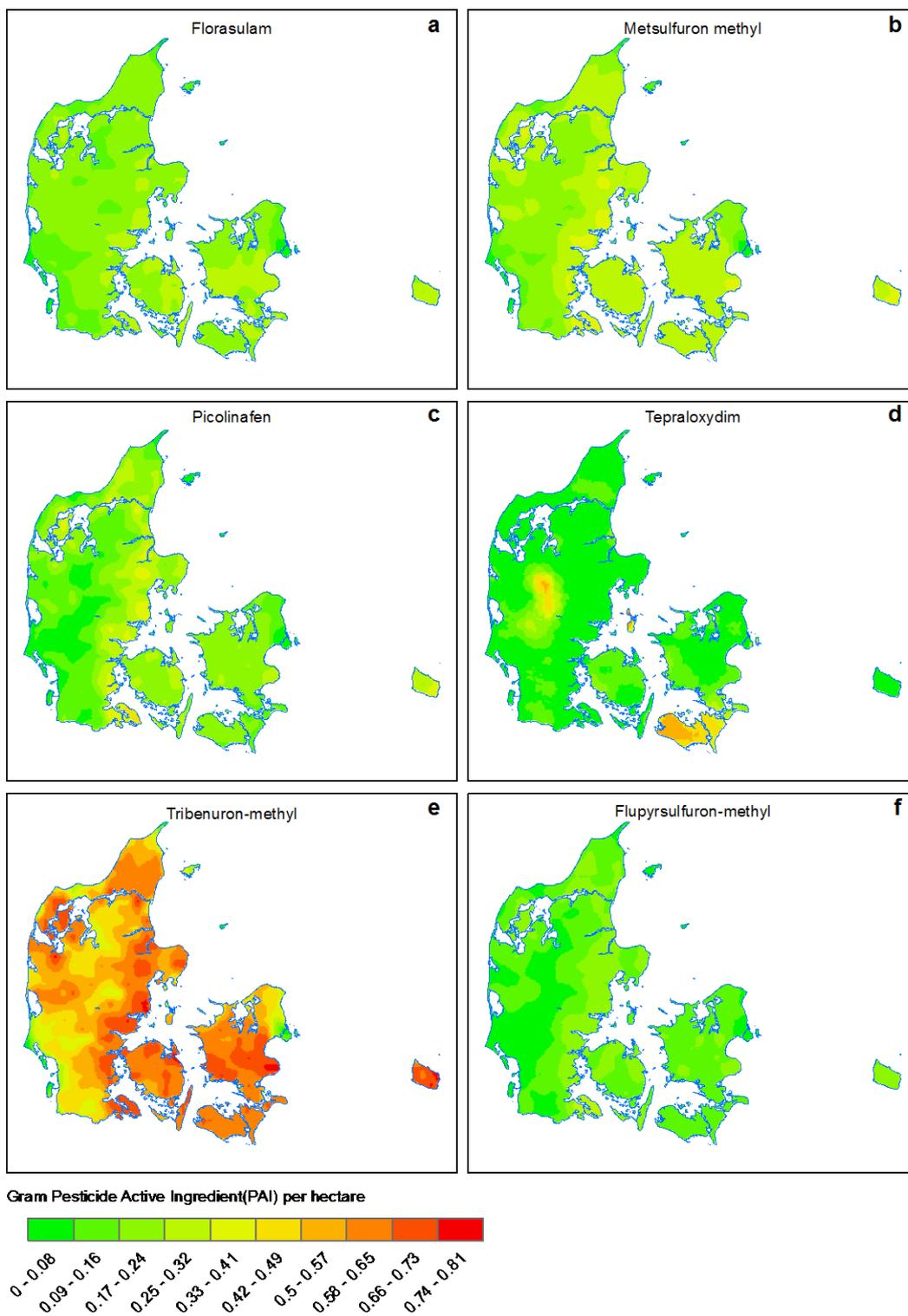


Fig. 7.2. Calculated mean doses of six herbicides.

Fig. 7.3 shows the results for the herbicides with max dose from 0.81 up to 2.83 g PAI ha⁻¹. Fig 7.3a represents mean dose of 2,4-D. This herbicide has been used in the years 2008 and 2009 with a total

mean use of 2324 kg PAI year⁻¹ and a mean dose of 0.84 g PAI/ha. The pesticide is used in spring and winter cereals, other seeds and in grass and clover. Normal dose is 1200g PAI ha⁻¹ for winter cereals, 800 g PAI ha⁻¹ for spring cereals, 1500 g PAI ha⁻¹ for other seeds and 2000 g PAI ha⁻¹ for grass and clover. The low total use and the different doses produce only a small regional variation in mean dose. The maximum dose is found to go up to 1.07 g PAI ha⁻¹.

Fig 7.3b represents mean dose of iodosulfuron-methyl-natrium that was used all year with a total mean use of 1365 kg year⁻¹ PAI and a mean dose of 0.49 g PAI ha⁻¹. This herbicide is used in spring and winter cereals, other seeds and maize. The normal doses are 10 g PAI for winter cereals and other seeds, 3.5 g PAI ha⁻¹ for spring cereals and 3 g PAI/ha for maize. The land use and different doses result in only small regional variations in mean dose. The maximum mean dose in certain regions is found to go up to 0.81 g PAI ha⁻¹.

Fig. 7.3c represents mean dose of rimsulfuron. This herbicide has been used in all three years with a total mean use of 202 kg PAI year⁻¹ and a mean dose of 0.07 g PAI ha⁻¹. The pesticide is used in potatoes only. Normal dose is 7.5 g PAI ha⁻¹ and the highest doses are found to go up to 1.38 g PAI ha⁻¹. The area with potatoes is primary located in the central part of Jutland near Karup where the highest mean dose is also found.

Fig. 7.3d represents mean dose of fenoxaprop-P-ethyl. This herbicide has been used in all years with a total mean use of 3290 kg PAI year⁻¹ and a mean dose of 1.2 g PAI ha⁻¹. The pesticide is used in spring and winter cereals. Normal dose is 69 g PAI ha⁻¹ for both winter and spring cereals and the highest doses are found to go up to 1.68 g PAI ha⁻¹. This pesticide is mainly used in areas with high potato production (Central Jutland), high vegetable production (Samsø) and regions with high sugar beet production (Lolland, Falster and Moen and the south part of Zealand).

Fig. 7.3e represents mean dose of propaquizafop. This herbicide has been used in all years with a total mean use of 2102 kg PAI year⁻¹ and a mean dose of 0.77 g PAI ha⁻¹. The pesticide is used in winter and spring rape, other seeds, potatoes, beets, peas and vegetables. Normal dose are 75, 150, 150, 125, 150, 100, and 150 g PAI ha⁻¹ for winter rape, spring rape, other seeds, potatoes, beets, peas and vegetables, respectively. The highest doses are found to go up to 2.72 g PAI ha⁻¹. As cereals are the dominating crops in Denmark the distribution generally follows the areas outside the dairy cattle areas in the south western- and north central part of Jutland.

Fig. 7.3f represents mean dose of bifenox. This herbicide has been used in the years 2008 and 2009 with a total mean use of 5664 kg PAI year⁻¹ and a mean dose of 2.06 g PAI ha⁻¹. The pesticide is used in winter and spring cereals, winter rape, and other seeds. Normal dose are 720 g PAI ha⁻¹ for cereals and other seeds and 360 g PAI ha⁻¹ for winter rape. The highest doses are found to go up to 2.83 g PAI ha⁻¹. As cereals are the dominating crops in Denmark the distribution generally follows the areas outside the dairy cattle areas in the south western- and north central part of Jutland.

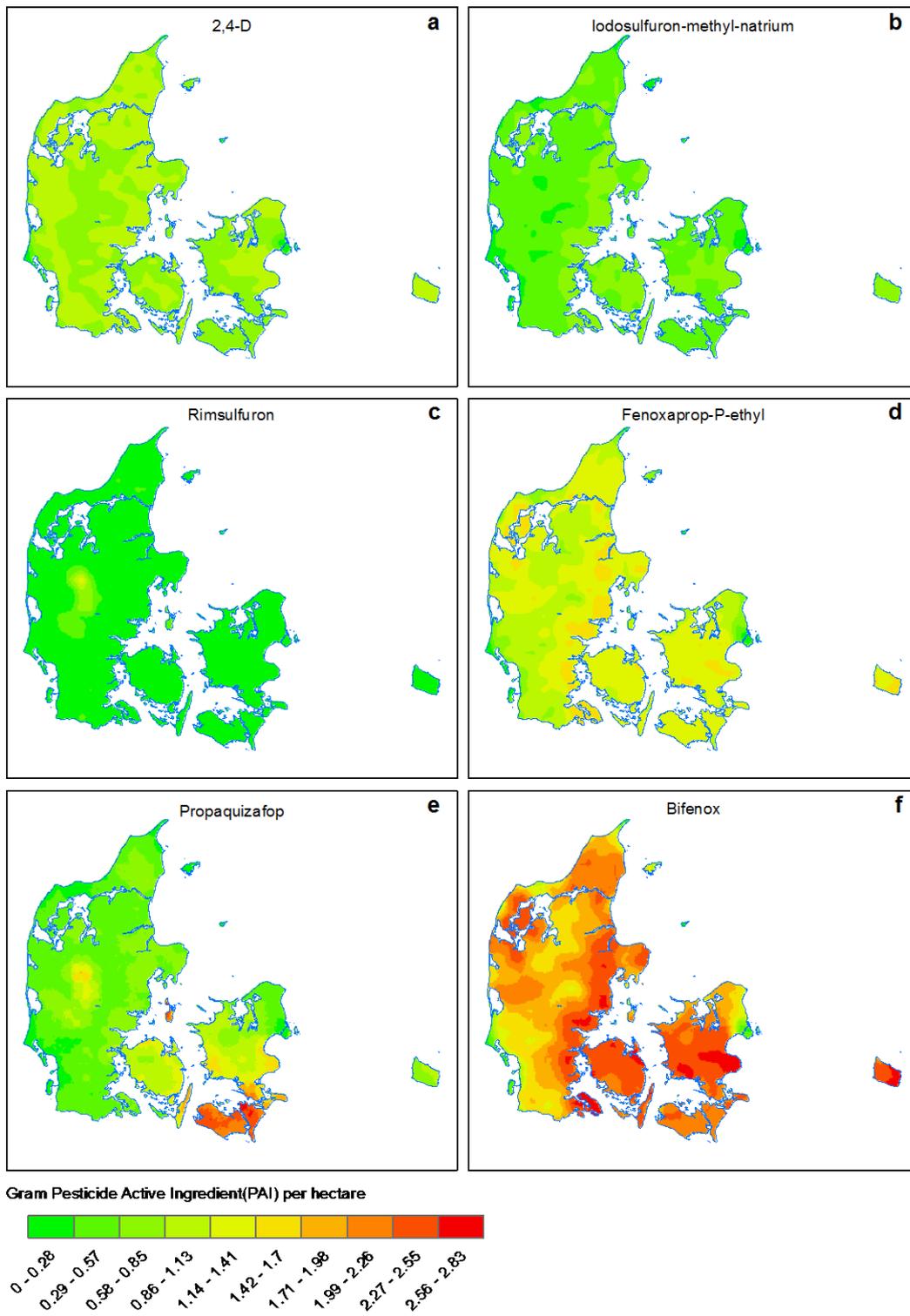


Fig. 7.3. Calculated mean doses of six herbicides.

In Fig. 7.4 is shown the results for the herbicides with maximum mean dose from 3.07 up to 4.64 g PAI ha⁻¹.

Fig 7.4a and 7.4d represent mean dose of fluazifop-P-butyl and cycloxydim, respectively. These herbicides have been used in all years with a total mean use of 2052 kg PAI year⁻¹ and 2772 kg year⁻¹ PAI, respectively. The mean doses are 0.75 g PAI ha⁻¹ and 1.01 g PAI ha⁻¹ for fluazifop-P-butyl and cycloxydim respectively. These pesticides are used in spring and winter rape, other seeds, potatoes, beets, peas and vegetable. The normal dose for fluazifop-P-butyl are 125g PAI ha⁻¹ for winter rape, 250 g PAI ha⁻¹ for spring rape, peas and other crops and 375 g PAI ha⁻¹ for potatoes, beets and vegetables. The normal dose for cycloxydim are 200 g PAI ha⁻¹ for winter rape and 500 g PAI ha⁻¹ for spring rape, peas and other crops, potatoes, beets and vegetables. For these pesticides the areas with highest doses are found in regions with high potato production (Central Jutland), high vegetable production (Samsø north of Funen) and regions with high sugar beet production (Lolland, Falster, Moen and the south part of Zealand).

Fig. 7.4b represents mean dose of forumsulfuron with is used in maize fields only. This herbicide has been used in all three years with a total mean use of 2708 kg year⁻¹ PAI, mean dose is 0.99 g PAI ha⁻¹. Normal dose is 90 g PAI ha⁻¹ and the highest mean dose goes up to 3.23 g PAI ha⁻¹. The area with maize is primary located in the south and western and central north part of Jutland with high dairy production (high share of green fodder crops).

Fig. 7.4c represents mean dose of clopyralid. This herbicide has been used in all years with a total mean use of 7903 year⁻¹ kg PAI giving an average dose of 2.88 g PAI ha⁻¹. The pesticide is used in spring and winter cereals, spring and winter rape, other seeds, beets, peas and grass and clover. The normal dose for clopyralid is 100 g PAI ha⁻¹ for winter and spring cereals and spring rape, 120 g PAI ha⁻¹ for winter rape, 150 g PAI ha⁻¹ for other crops, beets and grass and clover. Although the variation in mean dose is relatively low, the areas with highest doses are found in areas with high sugar beet production (Lolland, Falster and Moen and the south part of Zealand)

Fig. 7.4e represents mean dose of triflusulfuron-methyl that is used in fields with beets only. This herbicide has been used in all three years with a total mean use of 534 kg PAI year⁻¹ and a mean dose of 0.19 g PAI ha⁻¹. Normal dose is 45 g PAI ha⁻¹ and the highest mean dose goes up to 4.64 g PAI ha⁻¹. The areas with highest doses are found in areas with high sugar beet production (Lolland, Falster and Moen and the south part of Zealand).

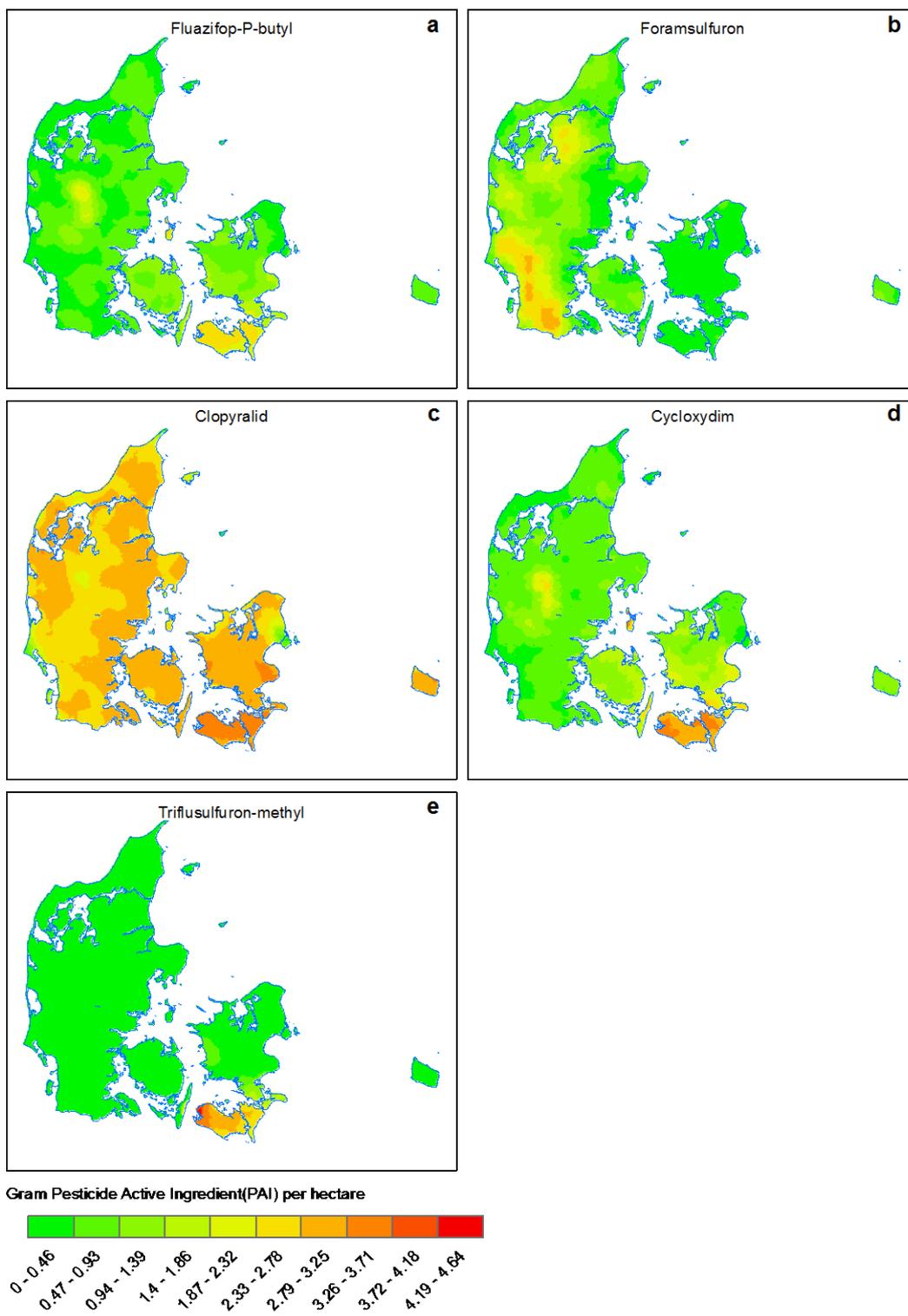


Fig. 7.4. Calculated mean doses of five herbicides.

In Fig. 7.5 is shown the results for the herbicides with max mean dose between 7.19 up to 9.31 g PAI ha⁻¹. Fig. 7.5a represents mean dose of desmedipham which is used in beets only. This herbicide has been used in all three years with a total mean use of 1088 kg PAI year⁻¹ a mean dose of 0.40 g PAI ha⁻¹ a maximum dose going up to 7.19 g PAI ha⁻¹. Normal dose is 720 g PAI ha⁻¹ and the highest mean dose goes up to 7.4 g PAI ha⁻¹. The area with highest doses is found in areas with high sugar beet production: Lolland, Falster and Moen and the south and western part of Zealand.

Fig. 7.5b represents mean dose of asulam which is used in fields with other seeds (mainly grass seed production). This herbicide has been used in all three years with a total mean use of 3242 kg PAI year⁻¹ giving a mean dose of 1.18 g PAI ha⁻¹. Normal dose is 800 g PAI/ha and the highest mean dose goes up to 97.2 g PAI ha⁻¹. The area with highest doses are found in areas western part of Funen, on the island Langeland (east of Funen) and on the southern part of Zealand and on the islands Falster and Moen.

Fig. 7.5c represents mean dose of clomazone which is used in fields with winter rape, other seeds and potatoes. This herbicide has been used in all three years with a total mean use of 8540 kg PAI year⁻¹ giving a mean dose of 3.11 g PAI ha⁻¹. Normal dose is 120 g PAI ha⁻¹ for winter rape and 90 g PAI ha⁻¹ for other seeds and potatoes. The highest mean dose goes up to 7.86 g PAI ha⁻¹. Locations with high doses are found in areas with other seeds as in the western part of Funen, Langeland, southern part of Zealand, Falster, Moen and in regions with a high potato production (Central Jutland near Karup).

Fig. 7.5d represents mean dose of mesotrione which is used in maize fields only. This herbicide has been used in all three years with a total mean use of 7060 kg PAI year⁻¹ giving a mean dose of 2.57 g PAI ha⁻¹. Normal dose is 150 g PAI ha⁻¹ and the highest mean dose is 8.62 g PAI ha⁻¹. The area with maize is primarily located in the south and western part of Jutland and in the central north part of Jutland with high dairy production (high share of green fodder crops (silage maize)).

Fig. 7.5e represents mean dose of diflufenican. This herbicide has been used in all years with a total use of 17395 kg PAI year⁻¹ giving a mean dose of 6.34 g PAI ha⁻¹. This pesticide is used in spring and winter cereals and in the category "other seeds", which primarily includes grass for seed production. Normal dose of diflufenican is 100g PAI ha⁻¹ for winter cereals and 75 g PAI ha⁻¹ for spring cereals and other seeds. This herbicide is used in all types of cereals and other seeds which give a very even distribution. Although it can be seen that the south western part of Jutland (sandy) with a high dairy production (high share of green fodder) has a lower mean dose compared with the rest of the country.

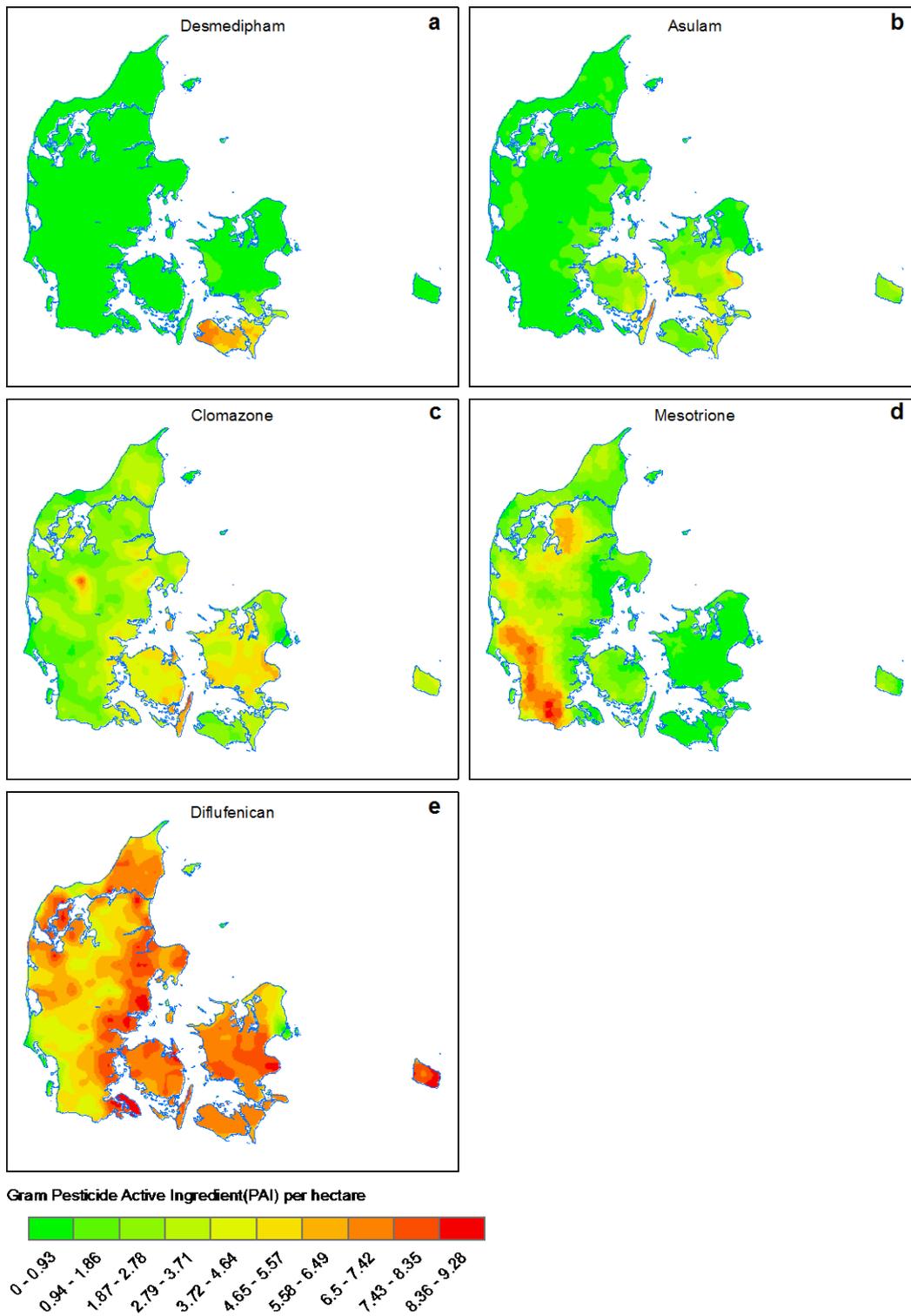


Fig. 7.5. Calculated mean doses of five herbicides.

In Fig. 7.6 is shown the results for the herbicides with mean maximum doses from 18.29 to 29.62 g PAI ha⁻¹. Fig. 7.6a represents mean dose of fluroxypyr which is used in fields with spring and winter cereals, other seeds, maize and grass / clover production. This herbicide has been used in all three years with a total mean use of 33004 kg PAI year⁻¹ giving a mean dose of 12.03 g PAI ha⁻¹. Normal dose is 144 g PAI ha⁻¹ for winter cereals and other crops, 126 g PAI ha⁻¹ for spring cereals, 270 g PAI ha⁻¹ for maize and 360 g PAI for grass and clover. The highest mean dose goes up to 12.1 g PAI ha⁻¹. This herbicide is used for cereals and other seeds, maize and grass and clover which give a relatively even distribution of the use in the country. Although it can be seen that the south western part of Jutland (Sandy) with a high dairy production (high share of green fodder (maize and grass/clover) have higher doses, compared with the rest of the country. This is primarily an effect of the higher recommended dose for maize and grass/clover.

Fig. 7.6b represents mean dose of bentazon which is used on fields grown with: spring cereals, other seeds, peas, maize and grass/clover. This herbicide has been used in all three years with a total mean use of 33745 kg PAI year⁻¹ giving a mean dose of 12.3 g PAI ha⁻¹. Normal dose is 720 g PAI ha⁻¹ for spring cereals, 1440 g PAI ha⁻¹ for other crops, 480 g PAI ha⁻¹ for peas, 500 g PAI ha⁻¹ for maize and 960 g PAI for grass and clover. The highest mean dose goes up to 20.0 g PAI ha⁻¹. The lowest mean dose is found in areas with high share of winter cereals which means the eastern part of Jutland and at Funen and Zealand.

Fig. 7.6c represents mean dose of bromoxynil, which is used on fields grown with: winter- and spring cereals, other seeds and grass/clover. This herbicide has been used in all three years with a total mean use of 47190 kg PAI year⁻¹ giving a mean dose of 17.2 g PAI ha⁻¹. Normal dose is 400 g PAI ha⁻¹ for all crop types. The highest mean dose is 21.6 g PAI ha⁻¹. This herbicide is quite evenly distributed over the agricultural area.

Fig. 7.6d represents mean dose of ioxynil, which is used on fields grown with: winter- and spring cereals, other seeds and vegetables. This herbicide has been used in all three years with a total mean use of 43700 kg PAI year⁻¹ giving a mean dose of 15.94 g PAI ha⁻¹. Normal dose is 400 g PAI ha⁻¹ for winter- and spring cereals, other seeds and 506 g ha⁻¹ for vegetables. The highest mean dose goes up to 22.5 g PAI ha⁻¹. This herbicide is quite even distributed in the country, although areas with high share of green fodder (south western and north central part of Jutland) generally have lower mean doses.

Fig. 7.6e represents mean dose of propyzamid which is used in fields with winter rape and other seeds. This herbicide has been used in all three years with a total mean use of 25731 kg PAI year⁻¹ giving a mean dose of 9.38 g PAI ha⁻¹. Normal dose is 500 g PAI ha⁻¹ for both winter rape and other seeds. The highest mean dose goes up to 29.6 g PAI ha⁻¹. The regions with highest doses are found in regions with a high crop share of especially other seeds, as in the western part of Funen, Langeland, southern part of Zealand, Falster, Moen, and Bornholm.

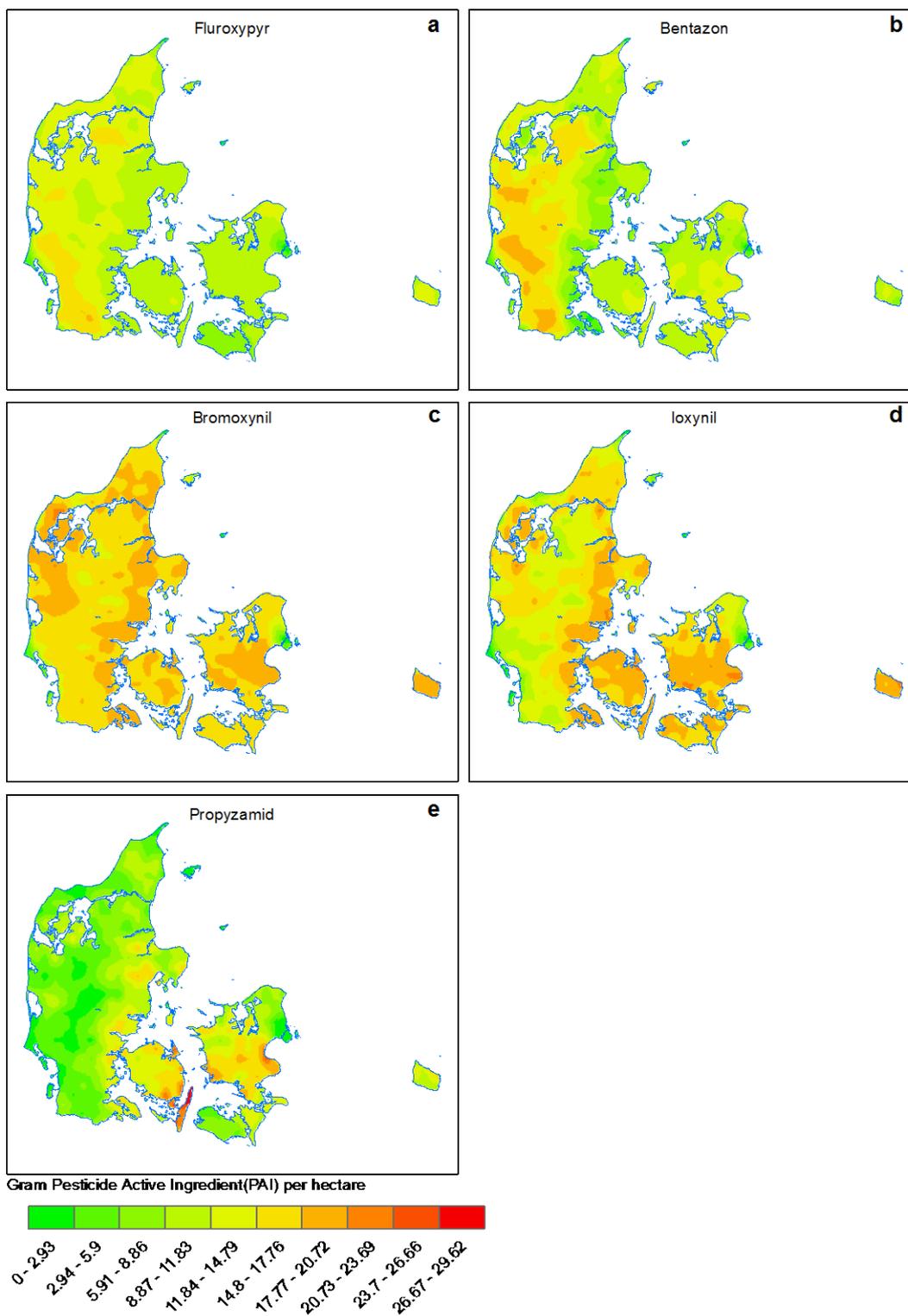


Fig. 7.6. Calculated mean doses of five herbicides.

In Fig. 7.7 is shown the results for the herbicides with maximum mean dose ranging from 45 g PAI ha⁻¹ to 86 g PAI ha⁻¹. Fig. 7.7a represents mean dose of ethofumesat which is used in fields with beets only. This herbicide has been used in all three years with a total mean use of 5853 kg PAI year⁻¹ equal to a

national mean dose of 2.13 g PAI ha⁻¹. Normal dose is 720 g PAI ha⁻¹ and the highest mean dose in certain regions goes up to 45.5 g PAI ha⁻¹. The areas with highest doses are found in areas with high sugar beet production: Lolland, Falster, Moen, and regions in the southern and western part of Zealand.

Fig. 7.7b represents mean dose of terbuthylazine which is used on peas and maize fields only. This herbicide has been used in two years (2007-2008) with a total mean use of 41668 kg PAI year⁻¹ giving a mean dose of 15.2 g PAI ha⁻¹. Normal dose is 420g PAI ha⁻¹ in peas and 1150 g PAI ha⁻¹ in maize. The highest mean dose goes up to 48 g PAI ha⁻¹. Maize is primary located on sandy soils in the south and western and central north part of Jutland, areas characterized by a high dairy production giving a high share of green fodder crops in agricultural land use. Peas are also primary grown on sandy soils, but have lower recommended dose and a minor share of the agricultural area, meaning that the area with maize is the dominating factor for the distribution.

Fig. 7.7c represents mean dose of phenmedipham which is used on other seeds and fields with beets. This herbicide has been used in all years (2007-2009) with a total mean use of 25348 kg PAI year⁻¹ giving a mean dose of 9.24 g PAI ha⁻¹. Normal dose is 720g PAI ha⁻¹ in seeds and beets. Max mean dose is 71.5 g PAI ha⁻¹. The area with highest doses is found in areas with high sugar beet production: Lolland, Falster and Moen and the south and western part of Zealand.

Fig. 7.7d represents mean dose of pendimethalin that is used at areas grown with winter- and spring cereals, peas, maize, and vegetables. This herbicide has been used in all years with a total mean use of 140745 kg PAI year⁻¹, giving a mean dose of 51.3 g PAI ha⁻¹. Normal dose in winter cereals is 1600 g PAI ha⁻¹, in spring cereals and peas 600 g PAI ha⁻¹, in maize 1600 g PAI ha⁻¹ and in vegetables 2000 g PAI ha⁻¹. The highest mean dose is up to 77g PAI ha⁻¹. This herbicide is quite even distributed, although areas with a high share of winter cereals have higher mean doses.

Fig. 7.7e represents mean dose of diquat-dibromide. This herbicide has been used in all three years with a total mean use of 22750 kg PAI year⁻¹ giving a mean dose of 8.12 g PAI ha⁻¹. The pesticide is used in peas and rape. Normal dose is 750 g PAI ha⁻¹ for other seeds and 1500 g PAI ha⁻¹ for potatoes. The highest dose goes up to 80 g PAI ha⁻¹. The area with potatoes is primary located in the central part of Jutland. Other seeds only have a minor effect on the distribution due to a more uneven land use distribution in the country.

Fig. 7.7f represents mean dose of MCPA which is used on fields grown with: winter- and spring cereals, other seeds, peas and grass and clover. It was used in all three years with a total mean use of 194374 kg PAI year⁻¹, giving a mean dose of 70.9 g PAI ha⁻¹. Normal dose in spring and winter cereals is 1500 g PAI ha⁻¹, 133 g PAI/ha in peas, 2000 g PAI ha⁻¹ in other seeds and 2025 g PAI ha⁻¹ in grass and clover. Highest mean dose goes up to 86 g PAI ha⁻¹. This herbicide is quite evenly distributed although in areas with a high share of beets and potatoes the doses are low.

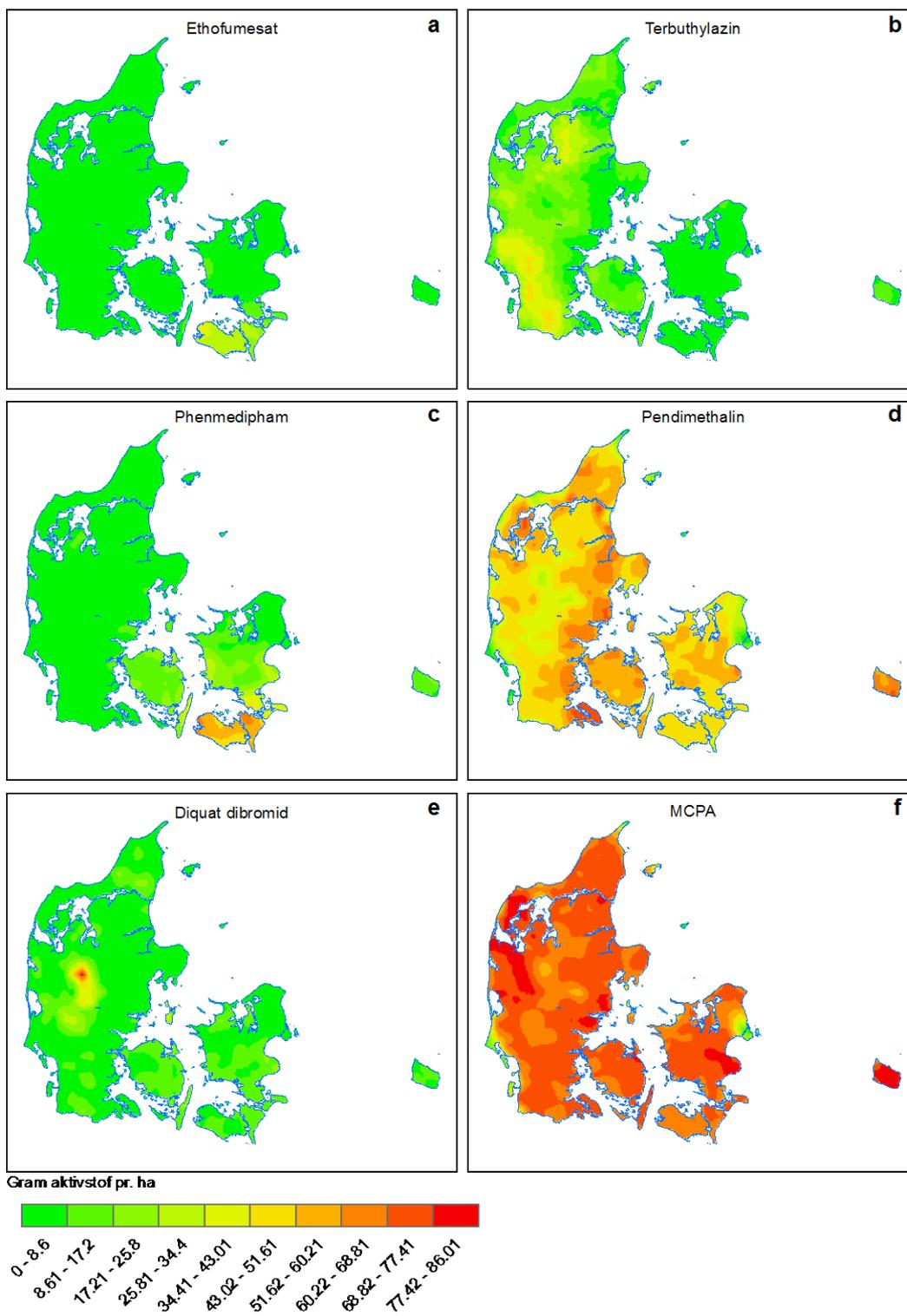


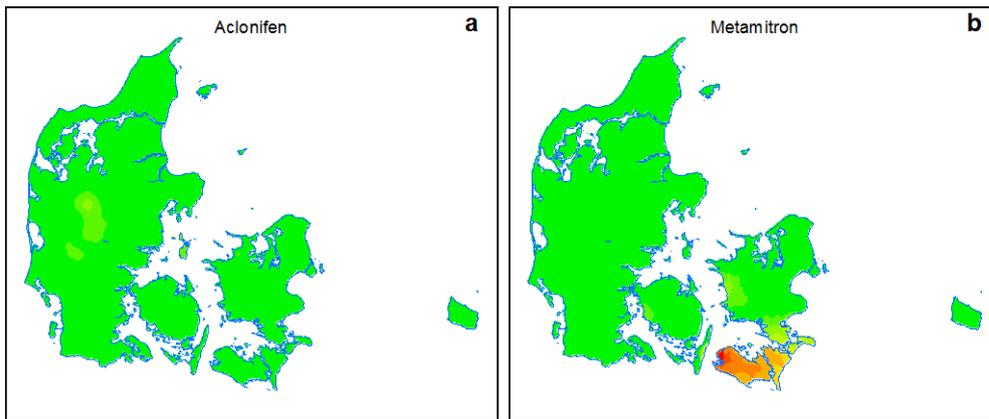
Fig. 7.7. Calculated mean doses of six herbicides.

In Fig. 7.8 is shown the results for the herbicides with highest maximum mean doses ranging from 104 g PAI ha⁻¹ up to 458 g PAI ha⁻¹. Fig 7.8a represents mean dose of aclonifen which is used in fields with potatoes, peas, and vegetables. This herbicide has been used in all three years with a total mean use of 23736 kg PAI year⁻¹, giving a mean dose of 8.65 g PAI ha⁻¹. Normal dose for potatoes and vegetables is 1500 g PAI ha⁻¹ and for peas the normal dose is 1200 g PAI ha⁻¹. The highest mean dose goes up to 104 g PAI ha⁻¹. The area with highest dose is found in the central part of Jutland near Karup, with a high production of potatoes. From the figure it can be seen that peas and vegetables do not affect the distribution so much, which is an effect of the width classes used in the legend of the figure.

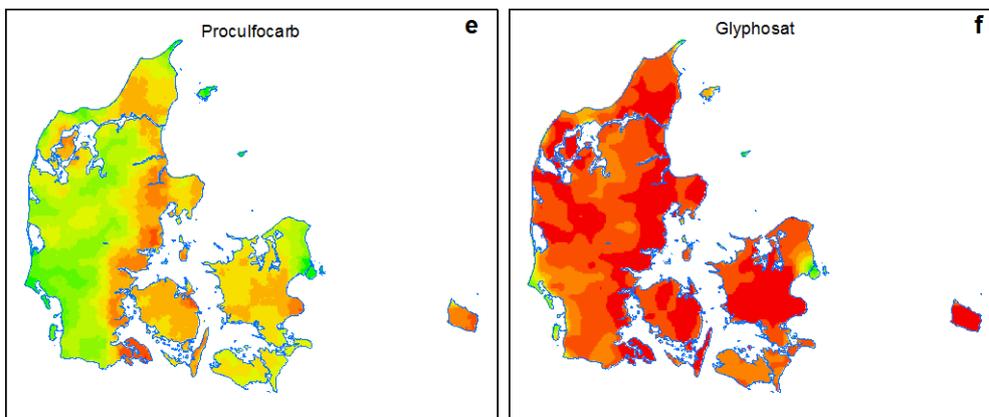
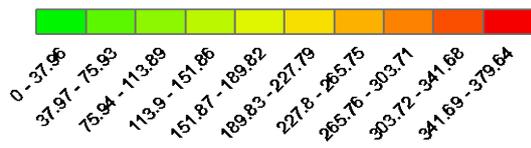
Fig. 7.8b represents mean dose of metatitron which is used in fields with beets only. This herbicide has been used in all three years with a total mean use of 50749 kg PAI year⁻¹ giving a mean dose of 18.5 g PAI ha⁻¹. Normal dose is 2100 g PAI ha⁻¹ and the highest mean dose goes up to 380 g PAI ha⁻¹. The area with highest doses is found in areas with high sugar beet production: Lolland, Falster, Moen, and the south and western part of Zealand.

Fig. 7.8c represents mean dose of prosulfocarb, which is used on fields grown with: winter cereals, other seeds and potatoes. This herbicide has been used in all three years with a total mean use of 629512 kg PAI year⁻¹ giving a mean dose of 230 g PAI ha⁻¹. Normal dose is for all crops are 2800 g PAI ha⁻¹. The highest mean dose goes up to 419 g PAI ha⁻¹. This herbicide is quite evenly distributed in the country, although areas with a high share of winter cereals have higher mean doses.

Fig. 7.8d represents mean dose of glyphosate which is used to control weeds in all types of crop types, except in permanent vegetation such as permanent grass. This herbicide has been used in all three years with a total mean use of 1093040 kg PAI year⁻¹ giving a mean dose of 399 g PAI ha⁻¹. Normal dose in all crops is 1260 g PAI ha⁻¹. The highest mean dose goes up to 458 g PAI ha⁻¹. This herbicide is quite evenly distributed in the country.



Gram Pesticide Active Ingredient(PAI) per hectare



Gram Pesticide Active Ingredient(PAI) per hectare

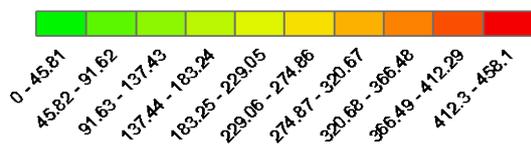


Fig. 7.8. Calculated mean doses of four herbicides. Two different legends are used for the maps. The maps a and b use legend range up to 379 g PAI ha⁻¹, and the maps c and c use legend range up to 458 g PAI ha⁻¹.

7.4.3 Discussion

The maps shown in Fig. 7.1 to 7.8 represent simulated mean annual results (herbicide doses) based on actual land use (arable land only). The simulated mean herbicide use is calibrated to match the PAI sold at national level. The 10 km grid cells have a mean agricultural area of 4930 ha, so often more than 20 farms are represented in the mean result. The results cannot be used at a smaller scale (field or farm scale) as the input data of the analysis and the methodology are not sufficiently accurate to apply at small scale. As the results are aggregated to 10 km square grid scale, we assume that the results give an overall good representation of the actual use.

The precision of the maps can be improved if it is possible to relate to the actual pesticide use or the quantities of pesticides that have been purchased by individual farms. This can improve the precision and make it possible to go from the 10 km grid scale to a lower scale such as 1 km grid scale or farm scale.

The results of the current mapping of the mean doses of different herbicides may potentially be used together with complementing information on soil types, soil adsorption/desorption characteristics, pesticide degradation characteristics, climate, and hydrology, to map areas with a potential high risk for pesticide leaching. Iversen et al. (2011) developed pedo-transfer functions for saturated and near-saturated hydraulic conductivity for soils across Denmark. Using these distributed data, combined with a recently developed raster-based soil property map, a new map for Denmark could be constructed for pointing out areas where macropore flow is likely and hence where there is a risk for leaching contaminants from the root zone.

The sorption-desorption characteristics are related to soil characteristics, especially to the soil organic C content, which has been mapped with the new raster soil maps for Denmark. Combining pesticide specific sorption characteristics (K_{oc}) and soil organic C maps, maps representing sorption characteristics can be used for creating new risk maps for leaching of contaminants from the root zone.

7.5 European initiatives

In parallel with the Danish initiatives, a European Committee initiative was launched in 1993 when FOCUS (acronym for the FORum for the Co-ordination of pesticide fate models and their USE) was formed. The remit of FOCUS was to develop consensus amongst the Member States, the European Commission, and industry on the role of modelling in the EU review process of active substances. Working groups within FOCUS were given a tight time schedule and within the following years several reports were published. FOCUS (1995) came up with the publication “Leaching Models and EU Registration”. The following year FOCUS (1996) presented “Soil Persistence Models and EU Registration” and “Surface Water Models and EU Registration of Plant Protection Products” was published in 1997 (FOCUS, 1997). Later (FOCUS, 2000) the working groups were concerned with providing tools for estimating environmental concentrations of active substances for the purpose of their evaluation for inclusion in EU positive list. Even though environmental fate models have been used for many years in a regulatory context, hence to describe the fate and behaviour of plant protection products and their metabolites in soil and water and use of mathematical modelling to *derive predicted environmental concentrations* (PEC) was seen as a critical step in the development of a harmonised EU approach. The targets set for the working groups forced the groups to review the literature and assess relevant models and model parameters, but also to draw from ongoing research in the different member states, and in other countries.

The EU runs a FOCUS home page (<http://focus.jrc.ec.europa.eu/>) where several work groups are presented: Ground Water, Surface Water, Landscape & Mitigation, Degradation Kinetics and Air. From the work groups Ground Water and Surface is given the currently approved versions of FOCUS simulation models (Table 1) and FOCUS scenarios that are recommended to calculate the concentrations of plant protection products in groundwater and surface water in the EU review process according to Council Directive 91/414/EEC.

The home page is active as News is frequently announced e.g. *11/Apr/2011 Assessing Potential for Movement of Active Substances and their Metabolites to Ground Water in the EU. The Final Report of the Ground Water Work Group of FOCUS, Sanco/13144/2010 version 1, 13 June 2009' is released. Along with the main report, the version control document 'Generic Guidance for Tier 1 FOCUS Ground Water Assessments version 2.0 January 2011' and the ground water download packages: FOCUSPEARL 4.4.4, FOCUSPELMO 4.4.3 and FOCUSPRZM GW 3.5.2 are also made available for use.*

Other important work is presented from the group Degradation Kinetics, which was active from 2002 to 2006. The group developed recommendations for calculating degradation kinetics in the registration process at EU and Member State level (FOCUS, 2006). The group highlights that degradation rates of active substances in crop protection products and their metabolites are among the most important parameters for assessing environmental exposure. Differences in approach can

substantially affect the degradation rates calculated from experimental data obtained in laboratory and field studies.

Table 1. Recommended models from the work groups Ground Water and Surface Water.

Work group	Ground Water	Surface Water
Model		
MACRO	✓	✓
PEARL	✓	
PELMO	✓	
PRZM_GW	✓	
STEPS_ONE_TWO		✓
SWASH		✓
PRZM_SW		✓
TOXSWA		✓

The international activities described above refer to the overall measure: The development of procedures and rules to harmonise the procedures within the EU for approval use of pesticides (the positive list Council Directive 91/414/EEC).

In a recently ended EU project FOOTPRINT (<http://www.eu-footprint.org>) the main objective was to create tools for pesticide risk assessment and management in Europe. The tools should be developed for use in three different user communities; a) farmers and extension service, b) water managers and c) policy makers. The risk assessment tools were based on existing pesticide fate models, and the project focused mainly on the model MACRO, which is the only model appearing as candidate in both FOCUS groups; Ground Water and Surface Water.

In the last decades common procedures for approving pesticides within the EU have been developed and attempts have been forwarded on modelling the risk for transport of pesticides to ground and surface waters.

8. Conclusions and recommendations

- Laboratory determined degradation and sorption/adsorption parameters based on international recognised batch standards are very important, e.g. it enables a comparison of characteristics among soils and pesticides. However, a direct use of these parameters in simulation models for describing the fate of pesticides at field scale may often show a bias in the calculated results. There is a need for more studies on undisturbed soils, e.g. monoliths sampled in the field and brought to the laboratory. Various test and modelling exercises can then be carried out to assess more field relevant parameters.
- Recent studies in field and in laboratory show that some pesticides may be adsorbed to particles and hence particle facilitated transport may increase the potential for leaching. However, this important transport path is not fully understood and it is important to implement this mechanism in commonly used models for pesticide transport.
- Particle-facilitated transport for strongly sorbing pesticides could be incorporated in models.
- On a field scale, the spatial variation of hydraulic, sorption and degradation properties (in macropores and in the matrix) can be considered by uncertainty estimation.
- Seasonal variability of the agricultural soil-plant system, and the short-term variability of rain intensity, need to be considered in adequate time resolution.
- Collecting farm data on pesticide use can qualify the mapping of risk for pesticides, given a possibility to make a more stratified sampling strategy for ground and surface water, to only look for pesticides/metabolites in areas where the pesticide are used.
- Inverse parameter estimation should ideally use all data (not sequentially use water, tracer, and pesticide data). As already pointed out, for assessment of pesticide properties, standard batch or incubation techniques are usually not representative of in-situ unsaturated matrix conditions, even if they (by volume) approximately represent the matrix.
- More studies could be identified based on the KUPA results. There is a need for models or information tools to point out risk areas for loss. Iversen et al. (2011) developed pedo-transfer functions for saturated and near-saturated hydraulic conductivity for soils across Denmark. Using these distributed data combined with a recently developed raster-based property map, a new map for Denmark could be constructed to point out areas where macropore flow is likely and hence where there is risk for leaching contaminants from the root zone.
- The precision of the maps of mean herbicide doses (Section 7) can be improved if it is possible to relate to the actual pesticide use or the quantities of pesticides that have been purchased by individual farms. Reporting of farm-based pesticide purchase can enable estimation of herbicide use at smaller scale (few km grid scale) or farm scale.
- The results of the current mapping of the mean doses of different herbicides (Section 7) can potentially be used together with complementing information on soil types, soil

absorption/desorption characteristics, pesticide degradation characteristics, climate, and hydrology, to map areas with a potential high risk for pesticide leaching.

- The sorption-desorption characteristics are related to soil characteristics, especially to the soil organic C content, which has been mapped with the new raster soil maps for Denmark. Combining maps on hydraulic data, pesticide specific sorption characteristics (K_{oc}) and soil organic C, new maps may be developed to present the risk of leaching of contaminants from the root zone.
- To investigate the complexity of transport of pesticides, we propose a new data sampling and modelling exercise based on new and existing field data. The simulation study is to be carried out at the PLAP sites (Silstrup and Faardrup). New soil hydraulic data are collected, and new pesticide kinetic data will be obtained using the new analytical laboratory equipment (Agilent 6224 LC-TOF) at Flakkebjerg, where a batch study will be carried out on repacked soil samples to assess degradation parameters of the pesticide compound fluzifop-P-butyl and its degradation product TFMP. The recognised MACRO model will be set up to simulate the fate of fluzifop-P-butyl and its degradation product TFMP.

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Zenilda L.C., Amauri G.S., and Leiliane C.A.A.2011. Analytical Methods for Performing Pesticide Degradation Studies in Environmental Samples. Pesticides - Formulations, Effects, Fate, InTech.

DCA - National Centre for Food and Agriculture is the entrance to research in food and agriculture at Aarhus University (AU). The main tasks of the centre are knowledge exchange, advisory service and interaction with authorities, organisations and businesses.

The centre coordinates knowledge exchange and advice with regard to the departments that are heavily involved in food and agricultural science. They are:

Department of Animal Science
Department of Food Science
Department of Agroecology
Department of Engineering
Department of Molecular Biology and Genetics

DCA can also involve other units at AU that carry out research in the relevant areas.

SUMMARY

The present study presents state-of-the-art description of transport and fate of pesticides (especially herbicides as they are by far the most used) when applied in the agricultural landscape. The main focus will be on the description of sorption and degradation and the transport of pesticides to ground water and surface waters. Pesticide leaching loss to the aquatic environment is strongly regulated by Danish Water regulations and the Water Framework Directive (tolerating an annual maximum average concentration of $0.1 \mu\text{g L}^{-1}$), however also other pathways for loss will be discussed. The present work will briefly present main knowledge gaps related to flow and transport of pesticides and present a catalogue of new research ideas.

To get a regional perspective on the risk for leaching of different pesticides from agricultural land, a number of information sources are found to be crucial. One main source is the actual use of the different pesticides. To provide a regional perspective on mean pesticide use we developed a method to estimate the actual mean pesticide use at regional scale based on actual land use. Based on this method, maps of mean applied doses of the different herbicides used in the years 2007-2009 in Denmark were calculated. These maps can be used as one of the sources to estimate the probability of leaching of different types of pesticides on a regional scale.