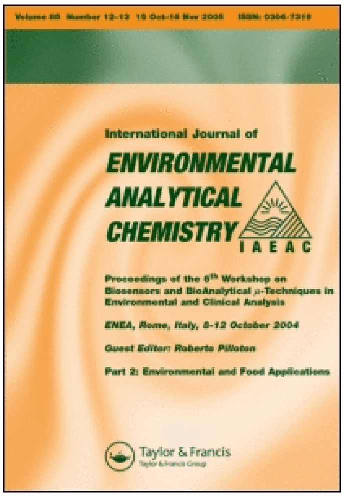

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Merete Styczen[a]
[a] DHI - Water and Environment, Hørsholm, Denmark

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DEVELOPMENT OF A TOOL FOR ESTIMATION OF PESTICIDE OCCURRENCE IN SURFACE WATER UNDER DANISH CONDITIONS

MERETE STYCZEN*

DHI – Water and Environment, Agern Alle 11, 2970 Hørsholm, Denmark

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The Danish Environmental Protection Agency initiated in 1998 the development of a modelling tool for estimation of pesticides in surface water in connection with registration of pesticides. The organisations involved in the development are DHI – Water and Environment, National Environmental Research Institute, Danish Institute of Agricultural Science (Flakkebjerg), and the Counties of Funen and Northern Jutland.

Two existing small 1st order catchments are chosen as basis for the scenarios. Models are calibrated and validated on existing flow and pesticide data for the two catchments. Finally, the models are modified to create scenarios for registration purposes. The approach differs from the more traditional approach where one field is placed along a stream and the main transport to the stream is expected to take place as drift into a more or less well defined amount of water. Considerable work has gone into the design of a suitable user interface including data input and extraction of data relevant for evaluation of effects.

Keywords: Pesticide; Modelling; Surface water; Registration; Catchment scale

INTRODUCTION

As part of the actions under Directive 91/414/EEC (Placing of Plant Protection Products on the Market), the authorisation of preparations containing an active substance entered on Annex I to the directive, is granted by the national authorities in compliance with the rules laid down in the directive. This authorization has to comply with the rules laid down in Annex VI of the directive, also known as the Directive of Uniform Principles.

One of the methods of assessment of pesticide fate is modelling. The Forum for the Co-ordination of pesticide fate models and their Use (FOCUS) have established guidelines for pesticide modelling (groundwater and surface water) within the EU, for evaluations related to Annex I [1,2]. Several EU-member countries use models for evaluation of pesticide transport to groundwater. In 1998, the Danish Environmental Protection Agency initiated the development of a modelling approach for estimation of transport of pesticide to surface water for Danish conditions.

*Fax: + 45-45-169292. E-mail: mes@dhi.dk

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The objective of the work is to produce a modelling tool that can be used by the Danish EPA with the data provided by the manufacturing companies to assess concentrations of pesticides likely to occur in streams and ponds after normal, legal agricultural use of the pesticide.

Initial Considerations Regarding Pathways for Pesticide Transport

Pesticides may arrive in a water body through (Fig. 1):

- direct spray drift from fields along the water body
- with wet deposition (in rain)
- with dry deposition
- dissolved in surface runoff
- sediment-bound with soil erosion
- with groundwater
- with drain flow, in dissolved form, or
- with drain flow, but bound to particles and colloids

The pesticide arriving in the drains and upper groundwater may have passed through the soil matrix or may have travelled through macropores.

Each pathway was reviewed with the purpose of judging which were important enough to be included in the model.

Spray Drift

Spray drift has traditionally been considered the most important entry route for pesticides to surface water. In the European context, the studies by Ganzelmeier *et al.* [3] are

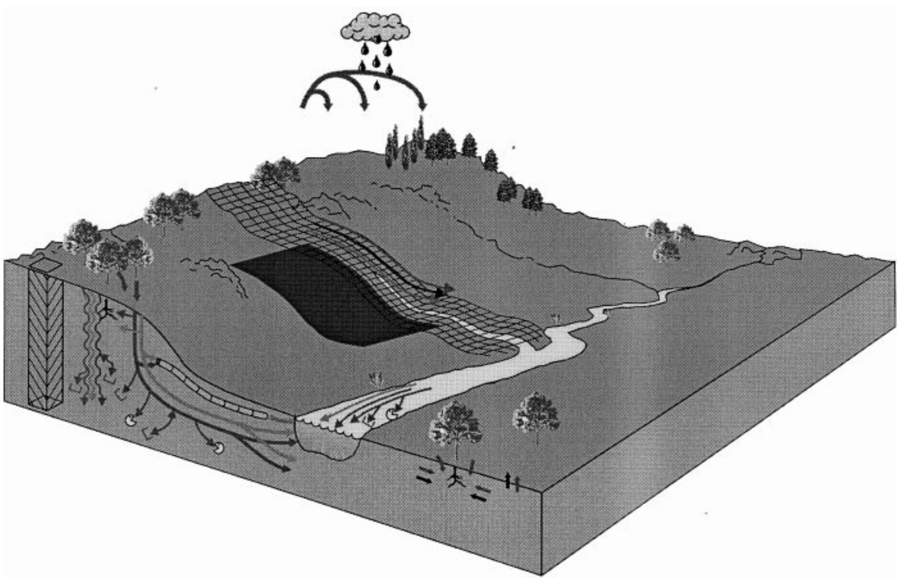

FIGURE 1 Pathways of transport of pesticides to surface water.

considered the best source of data concerning field spraying of annual crops under optimal conditions. One meter from a field with arable crops, up to 5% of the sprayed amount may deposit, but the drift falls exponentially with distance. Approximately 0.1% (0.03–0.3%) of the sprayed amount is registered at 10 m distance from the sprayed area. For fruit trees, the mean deposition is 1.8–5.7% depending on growth stage, at a distance of 10 m. The mentioned drift values are found on a flat field and with a windspeed of maximum 2 m/s. Under Danish conditions, the average wind speed during the spraying season is about double (Fig. 2), even in early morning hours, where farmers spray. Assuming that drift increases linearly with wind velocity at velocities greater than 1 m/s, wind velocities of 3–4 m/s results in drift values which in average are at the level of the Ganzelmeier 95% fractile for arable crops [4]. Wind direction is an important determinant of the actual exposure taking place.

Near streams, the sedimentation conditions for drift will be different from those on flat land. In Holland, Porskamp *et al.* [5] measured 30% less pesticide sedimentation at the water level than at the field level.

The potential of the process for pollution is considerable, particularly during a low-flow situation in the summer. In practice, few measurements of relevance to Danish conditions substantiate this. Kreuger [6] concludes that wind drift had little or no influence on stream water quality in the Vemmenhög catchment in Sweden. Only in one occasion during the four years of measurements could an increased concentration in the stream be related to spraying of adjacent fields, resulting in a stream concentration of 5 μg/L. This was, however, by far the highest concentration detected of this pesticide. For considerable periods every year, sampling was continuous.

Similar results are found in the county of Funen, where few pesticides are recorded in stream flow during dry weather. One event, however, gave rise to a concentration of

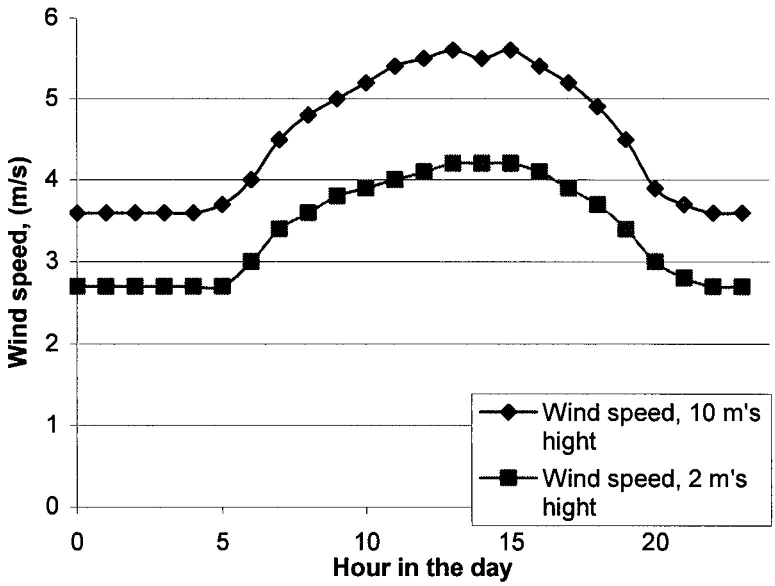

FIGURE 2 Wind profile near Flakkebjerg, Denmark, in May and June. Average from 1991–2000 [4].

9.8 μg/L (Rikke Clausen Schvaerter, pers.com, on review of data from [7]). Events could have been missed due to the sampling technique. The duration of a peak occurring from spraying of 100 m field along a stream is in the order of one minute.

In Denmark, stretches of streams are often (but not always) culverted or shielded from fields by trees, bushes or meadows.

Wet and Dry Deposition

Wet deposition does, in general, not occur as a function of local spraying. It is thus not relevant for the registration model. Felding and Helweg [8] found maximum concentrations of 0.2–0.4 μg/L in the month of October at three different localities in Denmark. A single observation reached 0.6 μg/L. Direct rainfall input may thus produce a measurable effect in the stream. A rough assessment may be made as follows: With a detection limit of 0.01, 0.2–0.6 μg/L require dilution by a factor 20–60 to become non-measurable.

Figures on dry deposition are rather uncertain. Results from ammonia indicate that up to 60% of volatilised or evaporated pesticide may be re-deposited within a few kilometres of the source [9], 40% deposits within the first 200 m. Felding and Helweg [8] conclude that the total deposition reaches 50–500 mg/ha/year (dry, wet, spray drift). In comparison to the total sprayed amount, it makes up approximately 0.01%.

Asman and Jensen [4] estimates that the possible air-related transport to stream due to dry deposition may reach up to 20% of the dose of very volatile compounds, assuming no resistance to deposition, 1.5 m non-spray zone and 1.5 m stream. For most pesticides, the dry deposition was estimated to be considerably smaller.

Pesticide Transport on the Soil Surface

Surface-related losses of 0.1–5% of the application are reported by Wauchope [10]. This includes both dissolved and particulate surface transport.

Overland flow amounts measured in plot studies in Denmark varies from negligible amounts, over 11–42 mm/year on the Ødum erosion plots to 41–163 mm/year on the Foulum erosion plots [11]. Only a few Danish figures are available regarding transport of pesticides with surface runoff. Felding *et al.* [12] carried out an experiment in the catchment of Syv Bæk, resulting in concentrations up to 6.15 μg/L, and losses of up to 0.08% of the applied amount.

No Danish figures are available regarding transport of pesticides specifically with erosion. The closest comparison possible is to phosphorus, which has been measured in plot studies in Denmark. Assuming that:

- the amount of active ingredient sprayed out is 1 kg/ha,
- the pesticide is distributed within the top 5 cm of the soil,
- the pesticide is not degraded before the erosion event,
- the enrichment ratio for the pesticide will resemble the one for phosphorus,

the losses in Foulum would be between 2 and 40 g of pesticide (of the 1 kg sprayed), and in Ødum between 0.5 and 5 g pesticide/ha/year, via the soil surface, or 0.05–4% of the sprayed amount. This equals a total concentration in the surface runoff of between 4 and 30 μg/L on both localities, but it varies with the year and the exact treatment of the soil surface.

Measurements on different slope units produced erosion figures from 0 to 25 t/ha lost to streams [13]. NERI estimates that about 3% of the Danish arable area are threatened by erosion. Serious events do not occur every year, but are mainly triggered by certain weather conditions, such as [14]: Large rainfall events (> 9–10 mm/day) followed by any intensity rainfall, low rainfall intensity over several days, rain on frozen soil or snowmelt, especially if the ground is frozen. Frozen soils or snowmelt only occur at minimum several months after application of pesticide.

Erosion is judged as a process that may be of local importance for transport of pesticide to streams, but it is not particularly widespread.

Transport in the Unsaturated Zone

From the soil surface to the saturated zone, the pesticide will be transported through the soil, either through the soil matrix or (in structured soils) through the macropores. Adsorption and degradation processes take place in this zone, particularly for pesticide transported through the matrix.

General findings for the unsaturated zone in Danish soils show that sandy soils may be described reasonably well with the traditional flow theory [15–17]. Solute transport follows the general convection–dispersion equations [18,19]. For the sandy loam soils, however, macropore flow is an important pathway e.g. [20–23]. While the flow through the matrix still behaves according to the traditional flow theory, the macropores allow high fluxes of water and solute to move quickly through the profile when local saturation occurs at the surface or in the profile (e.g., on a plough pan). The interaction between the solute and the soil is limited for the macropore flow.

Adsorption and degradation take place in the unsaturated zone. Degradation rates generally decrease with depth [1], and macropores may thus act to move pesticide to layers with low degradation rates.

A study of pesticide in soil moisture (extracted with suction cups at a depth of 80–90 cm) was carried out in Bolbro Baek and Højvads Rende by Spliid and Mogensen [24]. The concentration range observed in the moraine soil around Højvads Rende was 0–0.29 and 0–1.36 μg/L in the sandy soil in Bolbro Bæk catchment. The frequency of pesticide observations was higher in the moraine soil than in the sandy soil. A total of 14 compounds were studied. (MCPA, 2,3-D, Mechlorprop, Dichlorprop and three of their metabolites, DNOC, Dinosep, Simazin, Atrazin, Bromoxynil, Ioxynil and Isoproturon).

Groundwater

The transport to surface water bodies via groundwater will, in most cases, take place through secondary groundwater. Concentrations reported in upper groundwater are generally in the order of 0.01–0.1 μg/L [25]. Groundwater will not play an important role for small streams in the moraine clay areas as base flow amounts are negligible, but it will be important for the background concentration in streams in sandy areas, as the proportion of base flow is large e.g. [26].

Pesticide Dissolved in Drain Flow

Studies of pesticide concentrations in drainage water in Højvads Rende show concentrations of dissolved pesticide between 0 and 0.27 μg/L [24,27]. These concentrations are low compared to the earlier mentioned soil moisture concentrations and to studies of macropore flow, and this may be due to the fact that the sampling was done at 14-day intervals. Peak concentrations in the drains may thus not have been caught.

The common picture of drained moraine soils are high-concentration peaks of solutes of short duration (minutes or hours) caused by macropore flow [23,28]. A peak concentration of 24.0 μg/L for prochloraz has been observed by Villholth *et al.* [29] and 12–13 μg pendimethalin/L has been observed in an ongoing study [30]. A general estimate of losses through drains is in the range 0.1–5% of the application [28].

Colloid-bound Pesticide in Drain Flow

Reported losses of particles through drains are between 15 and 3010 kg/ha/year [31–35]. The total losses of hydrophobic pesticides in two reported studies were between 0.001 and 0.2% of the applied pesticide [29,32]. Between 6 and 93% of this was sediment bound.

A quantification of the importance of drains for addition of fine particulate material to the streams has shown that the drains on average contribute 29% of the transport, and in single intense rainfall events up to 70% of the total load to a stream [36]. The 6% loss in the sediment phase found in [29] was associated with a load of sediment of only 50 g/ha/mm rainfall, which amounts to approximately 35 kg/ha/year. Laubel *et al.* [37] found a loss of 120–440 kg/ha/year on the same site during other periods. The pesticides used in [29, prochloraz] and in [6, trifluralin] had similar sorption constants (K_{oc} of approximately 10 000). The 93% recovery in the particle phase observed by Brown *et al.* [32], however, may be overestimated as trifluralin is relatively volatile and hence a significant fraction of the dissolved pesticide may have been lost.

A comparison of erosion rates and loss of sediment through drainage may be difficult because it depends on many local factors, e.g. slope, infiltration capacity, soil cover, tillage, etc. Locally, erosion rates may be very high (3–10 t/ha/year has been reported from plot studies, up to 25 t from slope studies). However, only about 3% of the country is considered threatened by erosion, and high erosion rates are not observed every year. Drainage generally contributes to stream flow from larger areas, including those more distant from the stream, and is a process occurring during longer periods of the year, every year. About 20% of the Danish area is drained. As sediment generators to streams, the two processes thus appear to be of the same order of magnitude. The fact that the enrichment ratio of pesticide is generally larger in the finer particles [38] applies to both processes. Particles moving to drains have been shown to most likely originate from the topsoil [37,39]. There is thus no reason to assume that the transport of pesticides with colloids is less important than the transport with erosion under Danish conditions.

Pesticide Concentrations Observed in Streams

Stream concentrations have been measured by Spliid and Mogensen [24], in a sandy loam catchment (Højvads Rende) and a sandy catchment (Bolbro Bæk). The conclusions were that the number of positive samples and the concentration levels were highest in the stream in the sandy loam area. Furthermore, for the sandy loam catchment, measured concentrations in the stream were higher than in the drainage water and the soil water. In the sandy catchment, the concentrations in soil water were generally higher than in the stream. The fact that there is a discrepancy between soil water (extracted by suction cups) and stream water content of pesticide in the sandy loam catchment was attributed in the article to preferential flow paths, which often are of great importance on these moraine soils. The highest concentration measured in the stream was 7.3 μg/L in the sandy loam area, and 0.66 μg/L in the sandy area.

Measurements in streams have also been carried out in Lillebæk brook (also sandy loam) and Odense Stream on Funen [7]. The timing of the events in Lillebæk and Odense stream shows a clear connection between the occurrence of high concentrations in the stream and rain events during the spraying season [7]. These observations indicate a close link to the macropore and drain flow on sandy loam soils (Table I).

In other Nordic studies maximum concentrations reported are generally between 1 and 10 μg/L, with some extremes, however, up to about 50 μg/L [6,40].

Pesticide Concentrations in Ponds

Spliid and Mogensen [24] sampled four ponds 5–9 times between November 1989 and December 1990. Most analyses were negative. The highest pesticide concentration recorded was 1.1 μg/L and thus lower than that found in the streams.

In a period from November 1990 until mid May 1991, VKI has carried out analyses for pesticides in biota and sediment in selected ponds. For most of the samples and pesticides, a content below the detection limit was found (0.5–50 μg/kg for sediment; 1–100 μg/kg for biota). Pesticides detected in sediment and biota were: propiconazol (3.2 μg/kg in sediment), metsulforon-methyl (56–170 μg/kg in sediment) and tribenuron (11 μg/kg in biota) [41–43].

Overview of Pathways

It was decided that all processes mentioned should be included at the initial stage of the project. Sub-projects were formed for quantification of deposition on the soil

TABLE I Maximum concentrations of pesticide recorded in some Danish studies

	Max. single concentration recorded in studies (μg/L)
Højvads rende	7.3
Bolbro Bæk	0.66
Lillebæk	10.0
Odense Å	1.0
Vejrum Bæk	7.0

surface, dry deposition and colloid transport to provide a better base for the final decision on inclusion into the model. Additionally, other sub-projects investigated stream and pond-processes and mesocosm studies to initiate the links between exposure and effects (Table II).

Conceptualisation of the Model

Based on the assessment of importance of processes, models, test sites and scenarios had to be defined. The scenarios are the conceptual sites where the pesticides are evaluated through a model simulation. A scenario must represent a set of typical Danish conditions, suited for evaluating risk of surface water contamination. The scenario is not necessarily identical to a site that exists in reality.

Issues of Scale

The issue of scale occurs in relation to

- the size of catchment to choose, and its properties
- which processes to include (relevant at the decided scale)
- the time resolution required for the model.

Starting with the scale of the processes, Table III highlights the main processes and the scale on which they are considered important.

From the scale of the processes alone, one could argue that if the only important processes are wind drift (deposition) and drain flow, the source calculation could be limited to a 200–500 m long field draining into, and providing all the water, for a stream. The width of the field will then depend on an accepted relation between catchment size and stream length. The key issue, however, is that if the field generates all the water to the stream, it is, in fact, a catchment.

In case of interactions between the secondary groundwater and the stream, the natural scale of the process is the catchment. A dynamic calculation of groundwater levels is possible only through a catchment simulation. This is also true for erosion events, which to a large extent will depend on local saturation under Danish conditions.

It was therefore decided to use two small 1st order stream catchments as the unit for modelling. The selected model systems are MIKE SHE [44], describing the overland flow, unsaturated and saturated zone and MIKE 11 [45] describing the river.

With respect to the time resolution, there is considerable discrepancy between what is possible in terms of modelling and what data are traditionally used for assessment of biological effects. The time resolution of the model output is mainly a function of the resolution of the meteorological data and can be very detailed, while the data for assessment of biological effects is usually based on evaluations after days of exposure. The initial wish was to evaluate peak concentrations at 0.1 h time steps, and a simulation period of 10 years to cover a range of weather conditions. The present experience is that the size of intermediate files generated by the programme may limit either the simulation period or the time resolution in the model.

TABLE II Summary of quantitative information on pathways

Pathway	*Concentration*	*Other units*	*Comment*
Spray drift	Can theoretically give rise to concentrations in the order of hundred μg/L, measurements support up to 10 μg/L	For agricultural crops, up to 5% at 1 m distance in average 0.03–0.3% of the application at 10 m distance.	Width of application is 24 m. Most relevant within a distance of 50 m.
Wet deposition	0.3–0.4 μg/L	< 0.3 g/ha/year	Dominantly long distance transport
Dry deposition		< 0.5% of the surface application	Relevant within a distance of max. 500 m. Few data to support the value
Total deposition		50–500 mg/ha/year, equal to about 0.01% of the surface application.	
Dissolved in surface runoff + soil erosion		0–5% of surface application	
With soil erosion	< 30 μg/L	0–4% of surface application	Estimated to affect max. 3% of the surface area
With groundwater	0.0–0.1 μg/L		Thinning effect
With drain flow, dissolved	< 24 μg/L	0.1–5% of surface application	
With drain flow, bound to colloids	1.4 μg/L (source)	0–0.2% of surface application. (Few studies)	Due to extent of the process, it may be as important as soil erosion

NB: Note that the figures given are not in all cases directly comparable, and that all processes do not have the same relevance for different pesticides.

TABLE III Main pathways and relevant scale for description of the process

Pathways	*Scale of relevance for a stream*	*Comments*
Spraying and deposition on the soil	Field scale	
Direct drift	Approximately 50 m on each side of the stream	
Deposition (local)	Approximately 500 m on each side of the stream	
Surface runoff*	Catchment issue	Usually localised events in time and space, but not necessarily related to a distance to the stream in a simple way
Soil erosion*	Catchment issue	Usually localised events in time and space, but not necessarily related to a distance to the stream in a simple way
Drain flow*	One drainage system (down to field scale)	
Groundwater (secondary)	Catchment issue	
Groundwater (primary aquifer)	Groundwater catchment for the primary aquifer	
Stream	Catchment scale	A minimum of 1 km length is required (expert judgement)

*Surface runoff and erosion will usually take place where drains are not present or during events where they do not function. It is more or less an "either/or" situation.

Selection of Catchments

Each scenario must have a defined topography and size, land use, soil type distribution, geology, etc, providing a full description of the parameters of relevance for the hydrology simulation as well as for the pesticide simulation. To ensure that the representation of the different processes match reality to the greatest possible extent, two existing catchments were selected to provide the basis for the parameterisation. By selecting existing small catchments, a number of subjective considerations were avoided, such as size of catchment for the stream, area contributing with surface flow, agricultural intensity, drainage intensity, groundwater influence on the stream etc.

The selection of catchments was based on information about soil type, geology, agricultural use, rainfall, and data availability. The major candidates for selection were the catchments which are part of the Danish monitoring programme. These were, however, originally selected based on groundwater considerations, and they do not cover the range of conditions of relevance for surface water contamination.

The catchments selected (Odder Bæk and Lillebæk, Fig. 3) represent

- moraine clay soils (Lillebæk, coarse and fine sand-mixed clay, with 10–15% clay and 0–30% silt). Moraine clay soils dominate on Sealand, Funen and the south eastern part of Jutland.
- Sandy soils (Odder Bæk, 0–5% clay and 0–20% silt). However, during the course of the project it has become clear that the soils are slightly more clayey (4.1–6.4% clay) in the topsoil and that lower horizons in part of the catchment are clayey. Geologically north Jutland is more complex and intermixed than western Jutland, but it was not possible to find a catchment with appropriate data there.

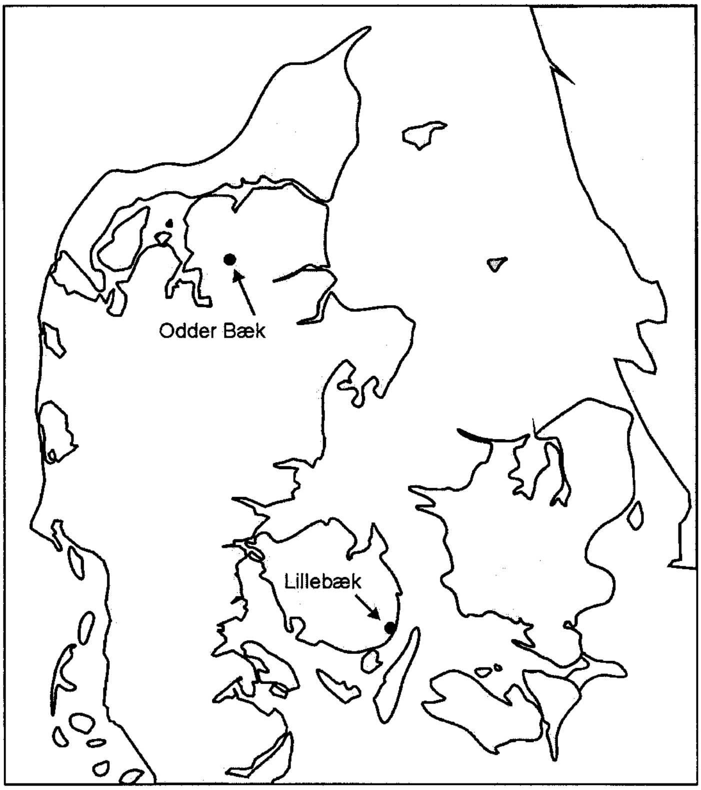

FIGURE 3 Location of the two selected catchments. Lillebæk represents moraine soil while Odder Bæk is a more sandy area.

Together, these texture types cover about 58% of the Danish arable area. Presently, no data sets exist on which to base a third stream scenario, representing soil types with higher risk of surface runoff and erosion.

Lillebæk is about 4.5 km^2, and Odder Bæk about 11 km^2. The average slope of both catchments is about 1.2%, but areas within the catchments may be undulating. More than half of Lillebæk stream is culverted, but about 1.8 km is open. Odder bæk is about 4 km long. Both catchments are described in Blicher-Mathiesen *et al.* [46], followed by yearly reports from NERI. Yearly reports of Lillebæk are produced by the County of Funen.

The model code has been undergoing validation on data from the two selected catchments. After this, the models will be modified to scenarios. The calibration model setup and calibration runs are reported by Thorsen *et al.* [47] and in [48] as part of the documentation to the model. The uncertainty estimations are discussed by Sørensen *et al.* [49].

Measuring Programme

A considerable amount of data is already being collected in the two catchments as part of the National Monitoring programme. The programme concentrates on water,

TABLE IV Existing monitoring sites in the two catchments

	Lillebæk	*Odder bæk*
Soil moisture stations	6	6
Groundwater stations	21	24
Drain stations	7	2
Stream flow stations	2	3, but only 1 after 1993
Weather stations	1	2, but 1 is not inside the catchment

TABLE V Number of samples for pesticide analysis for each catchment, total for the two years measurement programme

	Lillebxk	*Odder bark*	*Experiment*
1. Atmospheric deposition	0	0	
2. Drift determined based on known spraying	10	10	
3. Drift as controlled experiment			20
4. Drains: pesticide loss during events	50	25	
5. Streams, pesticide loss during events	50	25	
6. Drains: pesticide loss, max. values	50	25	
7. Streams: pesticide loss, max. values	50	25	
8. Groundwater: determined through baseflow	12	12	
9. Surface runoff and erosion, covered by 5 and 7	–	–	–
10. Stream sediment, pesticide content	10	10	
11. Pesticide fate in the stream	13	13	
In total	232	132	20

nutrients and pesticides, but the intensity of pesticide measurements was too low. Additional measurements were thus planned for two drain stations and two stream flow stations in Lillebæk and for one drain station and one stream flow station in Odder Bæk (Tables IV and V).

The total number of samples to be analysed was limited by the budget of the project. Samples were selected to cover specific events and for a number of events, samples were pooled over the event to minimise analysis costs.

Details of the Scenario

The major features of the catchment, such as size and topography will be unchanged in the scenarios. The stream will be unchanged with respect to length and roughness due to vegetation. In both cases, the streams are small 1st order streams, and considered to be representative of the types of streams where pesticides are found in the highest concentrations. However, part of the Lillebæk brook is piped. In the scenario, the whole stream will be simulated as open.

Agriculture makes up 98% of the Odder Bæk catchment and 89% of Lillebæk catchment. In the catchment of Odder Bæk, the remaining 2% of the area is forested, and 12.9% of the agricultural area is covered by permanent grass. In Lillebæk, 2% is forest and 9% is villages and roads. In a model set-up, some of the roads are likely to disappear, so the agricultural area is likely to take up a little more land in the model than in reality. Both cases are very realistic of intensive agricultural areas in Denmark, with the sandy areas being more sparsely populated.

The overall land use of the catchment will be maintained in the scenarios. Although the permanent grass area appears large in the sandy catchment, similar permanent grass areas are found in other sandy areas of Jutland. For the counties of Sønderjylland, Ribe, Ringkøbing, Viborg and Nordjylland (dominated by sandy soils), the percentages of permanent grass are between 14.5 and 18.2. Thus, 12.9% is therefore not unrealistic, in fact being slightly less than average.

It has been expressed clearly from the EPA that in the scenarios at tier two, which the model is being developed for at present, all arable land should be covered with the crop to be tested, and all should be sprayed with the compound to be tested. In Lillebæk, the actual usage pattern shows that some pesticides are used at up to 70% of the area in a given year.

A decision to include the permanent grassland as arable agricultural land would affect the simulations considerably, as these grassed areas usually are found near rivers, in areas with high groundwater, and thus highly susceptible to leaching. Additionally, they limit the area from where drift can occur. Usually, these soils are not suitable for cropping. These areas are not sprayed in the scenarios.

A recommended change, however, is to "remove" the tree barrier found along most of the length of Lillebæk in the scenarios. The reasons for this are (1) that the degree of shielding of this particular stream is higher than what is generally found, and (2) there are no figures for wind drift through that type of barriers. However, the width of non-cropped buffer zones are kept.

The definition of a pond turned out to be more complicated than that of a catchment, particularly with respect to hydrology. The ponds must be small. On sandy soils, the available material shows a typical size of 300–500 m^2, on sandy loam, the size is about 200–400 m^2 [50]. The depth of the pond is determined by the requirements that:

- it should not dry out, and
- a typical variation of the water level in small ponds is about 1 m.

A depth of 0.5 m at minimum would then mean a typical depth of 1.5 m during the wet parts of the year. The variation in depth is then from 0.5 to 1.5 m. The topography follows the landscape in the catchment, and some macrophytes must be included. It was decided to select existing ponds in the catchments and shape them in the model to fit the requirements. For the moraine area, the pond is filled with surface water or drainwater and water drains to lowerlying groundwater. In the sandy area, the pond is influenced directly by groundwater.

The pesticide will be applied every year during the simulation period, which is expected to be 10 years. Several applications in a year are allowed. Because the result of a simulation is highly dependent on the date of application selected and the time between this date and the first rain, the model should be run with different application dates. The model will be able to take into account that spraying does not occur during rain events.

For the moraine scenario, special considerations must be given to the rainfall input, as macropores are considered an important pathway. Detailed intensity data is not available for the location from 1989–1999, but stations with intensity measurements are available relatively close by. The rainfall pattern at several of the intensity stations was compared with data from the rainfall station in Lillebæk catchment (daily values for most of the period), and one of these (Odense, 28184) was selected as the best substitute for the local rainfall series in the Lillebæk scenario.

The pathways and process descriptions are summarised in Table VI.

TABLE VI Overview of process descriptions and parameterisation

Pathway	*Process*	*Description*	*Parameterisation*
By air	Drift	Based on Gazelmeier, but adjusted for wind-speed (3–4 m). Special values derived for Spruce trees. The pesticide arrives in the stream within one minute/100 m.	The buffer zone can be set by the user. However, existing non-cropped zones are represented in the model.
	Dry deposition	Method developed by Asman *et al.* [4] taking into account the length of the sprayed area and the width of the buffer zone, the surface conditions where the spray falls, and the conditions of the stream. The dose is received by the stream uniformly over 7 days.	The length of the sprayed area is given by the existing land use. The buffer zone can be set by the user. However, existing non-cropped zones are represented in the model.
Along the soil surface	Dissolved	Hardly any surface flow takes place in any of the models	Not individually parameterized
	Erosion	No erosion takes place in the model	–
Through the soil	Deposition on the soil	Based on recommendations from [1] except for winter wheat, barley, potatoes and sugar beet, where local values are available [51]	Depends on crop selected
		The dosis given to bare soil is corrected for drift and dry deposition losses.	Depends on crop selected
	Dissolved in the unsaturated zone	The description follows what is described in [22]. In Lillebæk, macropores are included, while Odder Bæk is without macropores. The model allows for sorption and degradation of pesticide (and metabolite) as well as formation of a metabolite.	Measured values of hydraulic parameters exist for six profiles and drainage catchments of each catchment. The parameterisation of the unmeasured values for the unsaturated zone follows the descriptions given by FOCUS for modelling of leaching to groundwater.

	Colloid-bound in the unsaturated zone	Follows descriptions by Villholth *et al.*, [29].	To be determined
Saturated zone	Drain flow	Refsgaard and Storm [44]. No processes take place during the transport in drains	
	Water flow	Refsgaard and Storm [44]	Based on local data (geophysics and borehole-data, as well as groundwater levels)
	Solute transport	Refsgaard and Storm [44]. Initially, no degradation is expected to take place in the saturated zone. Colloids not transported through drains are caught. Model-wise, sorption is possible in this zone.	Based on values for similar soil types from earlier studies.
Rivers, ponds	Water flow	Wium *et al.* [45]	Based on local data (cross sections, flow measurements)
	Advection/dispersion	MIKE 11 technical documentation	Local dispersion experiments were carried out.
	Processes	Description developed for the project. It includes hydrolysis, photolysis and biodegradation under aerobic and anaerobic conditions. Sorption takes place to sediment and macrophytes [52].	[49,52].

More details of the scenarios and the reasoning behind them is available in the Inception report and first two status reports [53–55] of the project.

User Interface

Due to the fact that the purpose of the model is registration and the user group cannot be expected to be full time modellers, the user interface is a particularly important part of the model. The user interface allows the user to select scenario (location, stream/pond and for ponds aerobic or anaerobic conditions of the sediment), and to specify crop, buffer zone width and pesticide properties. The model allows one metabolite. The user cannot change the hydrological simulations which are pre-run and are used as input to the solute transport calculations (Fig. 4).

The user specifies pesticide (and metabolite) parameters such as time of spraying, dose, Koc (or Kom, or Kclay), DT_{50} in soils calculated according to the FOCUS recommendations [1], molecular weight, Kow, Henry's law constant, pKa-values, degradation parameters for hydrolysis, and photolysis and results from degradation experiments in water/sediment [52] under aerobic and anaerobic conditions. Specifically for the metabolite, parameters specifying the formation rate from each degradation process have to be given.

Help is available for every menu, assisting the user in defining input.

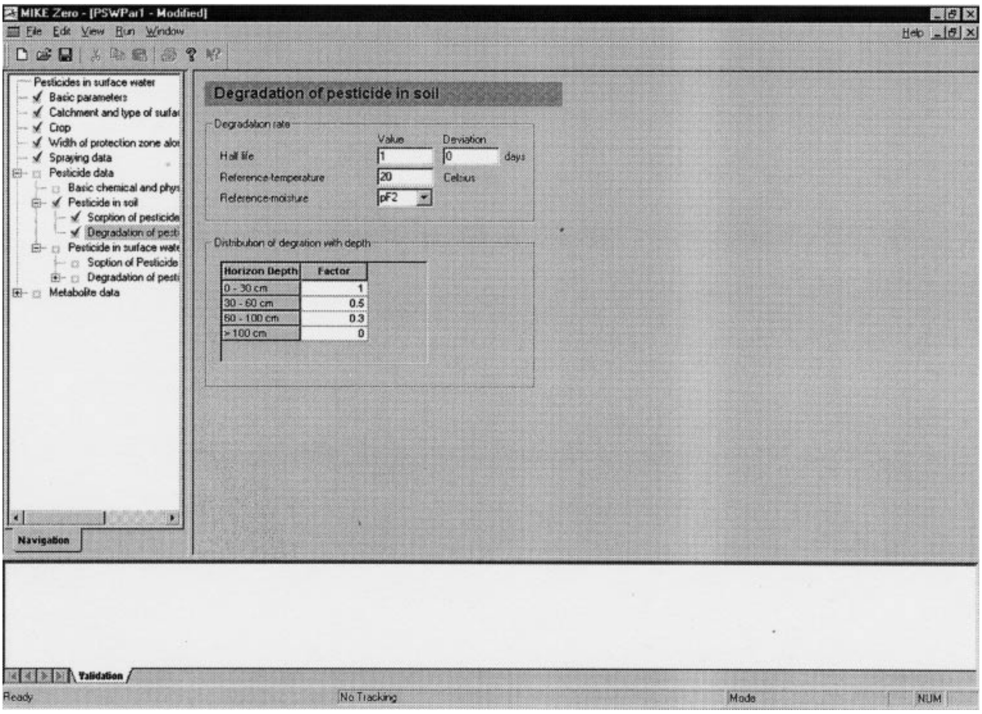

FIGURE 4 Example of menu for the PestSurf programme. The field to the left shows an overview of all menu pages, the navigation field in the bottom displays error-messages if data are missing or not entered correctly.

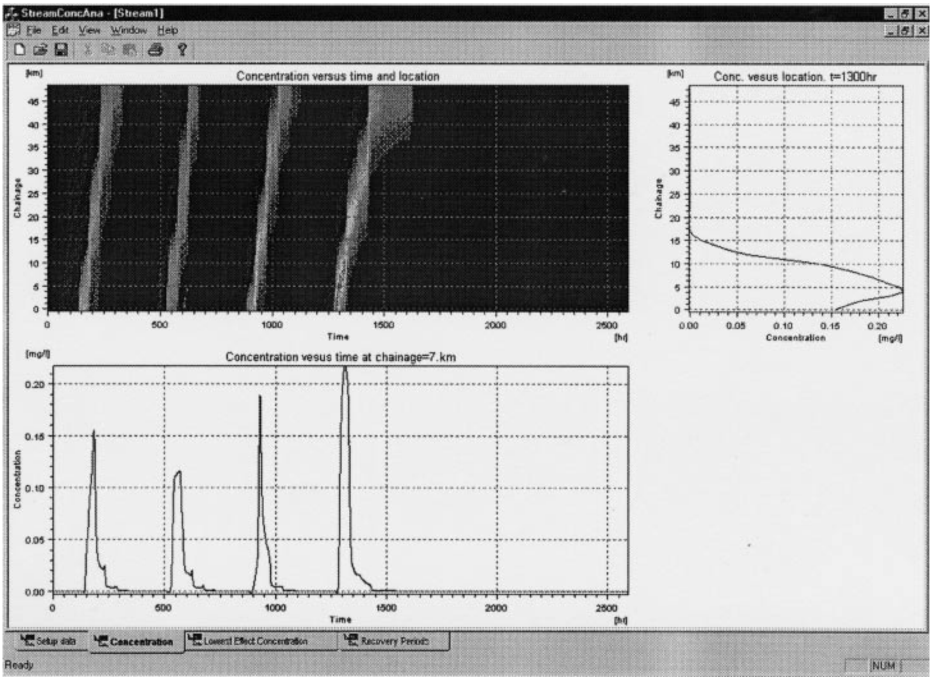

FIGURE 5 Example of plot showing concentrations of pesticide moving through the stream. The *y*-axis on the top left plot shows the length of the stream.

Specification of output requirements has been an important and time consuming step. This has been complicated by the fact that the majority of work on biological effects of pesticide exposure has been done in ways that make the results difficult, if at all possible to transfer to the exposure situations generated by modelling of streams.

An overview of the results is provided by the plot shown in Fig. 5, showing the time on the *x*-axis, the length of the stream on the *y*-axis and the measured concentrations in colour. Results can be screened by defining a minimum value that should be shown on the plot (typically a value defined on the basis of toxicity).

Several tables will be generated, comprising information on events defined as occurrence of concentrations above a certain limiting value. Events are defined through their duration, their maximum value and the time until the next event occurs.

Frequency distributions will be made on the max-values of the events and the duration of events.

Running averages over time will be generated, to allow comparison with standard values of toxicity over 24, 48, 72 h etc.

CONCLUSION

The project is non-traditional in several ways. It works with catchments instead of "edge of field"-scenarios, and all scenarios are hydrologically consistent. It deals with ponds and streams instead of only ponds, as has been the traditional approach. A very important consideration has been to avoid defining the "worst case" situation through selection of estimated "worst case" inputs. First of all,

all pathways can never be "worst case" at the same time, and secondly, even for groundwater simulations, experience has shown that the interactions between climate, soil, pesticide and time of application are such that a single worst case scenario does not exist.

The described model is well underway and is expected to be operational by late 2002. Three problems, however, still require considerations.

The original aim was to run the model for 10 years, but at the same time work with a very fine time resolution on concentrations. To speed up the simulations, flow calculations were to be done in advance and used as base for the solute transport calculations. The effect of this is the generation of very large intermediate files, and although work has led to a compression of these files by a factor of 5–6, the generated files are still very large. The result may be to reduce the period of simulation in order to obtain the required detail in the simulation.

The second problem is the interpretation of results. As mentioned above, the traditional methods used in assessment of biological effects investigate a closed system and assess mortality/effects after rather long time periods. Particularly for a stream, the observed peaks may be of rather short duration, and the exposure pattern is thus different. The Danish EPA has, in consequence, initiated a number of projects studying effects of these shorter exposures. An ongoing debate is which concentrations are of most relevance. For some organisms, concentrations in sediment may be considerably more relevant than the concentrations in water, and for some organisms, the concentrations on macrophytes may determine their actual intake.

The third problem encountered is that the results of the first simulations have shown that the major events measured must be due to pollution from point sources. This places a questionmark on the interpretion of the original review. Studies of drains without point sources show maximum concentrations in the order magnitude of 10–20 μg/L. Stream concentrations of 1–10 μg/L require such high concentrations from the majority of the catchment. However, when such high concentrations are found of pesticides used on only one or a few fields in the catchment, calculations of dilution show that the concentrations under the field should have been in the order of mg/L. Such high concentrations have not been found under fields or in drains. Leaching from point sources takes place during flow events just as from field application. In the investigated cases, which represent the three highest pesticide peaks measured in Lillebæk during 1999, spray drift could be ruled out. Furthermore, more than 50% of the registered peaks (defined as an event with a concentration greater than 0.1 μg/L) are caused by these three pesticides or their metabolites, indicating a pool of the pesticide being washed out over time.

The review may thus have overvalued the transport of pesticide from field applications through drains as a source of high concentrations in the stream. Although point sources are outside the scope of the registration model, this implies that some attention should be directed towards limiting the creation of point sources through the handling of pesticides on the farms.

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