

**Catchment monitoring for pesticides – Unilever Colworth sustainable agriculture project**

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**ABSTRACT**

Agrochemical concentrations, including pesticides, were measured at a number of automatically sampled drainage and streamflow monitoring stations established within a 60 ha arable sub-catchment on the Colworth estate, Bedfordshire, UK. Monitoring was conducted as part of an integrated programme evaluating the arable system impact on the environment, with the aim of developing a sustainable management policy by adoption of new cropping and cultivation practices. In this first year little pesticide was detected in leachate from the study area before spring pesticide applications to the mainly winter wheat crop. Pesticide concentrations in spring runoff events measured at the catchment outlet were highest for the conazole fungicide tebuconazole ( $1.3\mu\text{g L}^{-1}$ ), and for the herbicides terbuthylazine and terbuthryn ( $0.21\mu\text{g L}^{-1}$  to  $0.91\mu\text{g L}^{-1}$ ) applied to a single field of peas. In early autumn drainage events, the diazinone herbicide bentazone, and the triazine herbicide cyanazine (applied the previous spring) were detected in leachate at concentrations  $6.0\mu\text{g L}^{-1}$  and  $1.4\mu\text{g L}^{-1}$  respectively, with total losses of 1.4 and 2.0% of active substance applied.

**INTRODUCTION**

The Unilever Colworth Sustainable Agriculture Project was established as part of Unilever's global sustainable agriculture initiative (see <http://www.unilever.com>). This approach is being undertaken utilising an existing well established farming system where the maintenance of stable crop yields to maintain profitability was an important factor, whilst seeking to reduce the overall environmental impact of the farming operation. Water quality sampling stations were established in support of the project in October 1999. In the first year of monitoring (1999 – 2000), baseline water quality data were collected from a number of monitoring points with the objective of characterising nutrient and pesticide losses within the study area, and quantifying losses originating from outside the study area. In subsequent years management of agrochemical inputs within individual fields will be modified to include sustainable treatments aimed at lowering environmental impacts and thereby the associated water clean up costs. These treatments, although not organic, are intended to be beyond current UK integrated crop/pest management (ICM, IPM) practices. The sustainable treatments will be paired with normal good agricultural practice (GAP) management within a split field approach. This paper reports the first year results from the baseline pesticide monitoring.

## **METHODS AND MATERIALS**

### **Site**

The 76 ha study area formed part of the Colworth estate, (Bedfordshire, UK) and consisted of a group of 8 arable fields, predominantly in winter wheat, but including one field of oilseed rape and one field of peas within the rotation. The predominant soil series was Hanslope, consisting of a clay loam soil over stony, calcareous clay. All the study fields had extensive under-drainage systems, with secondary drainage treatments consisting of either mole drainage or subsoiling. All field drains eventually discharged into a main stream running through the centre of the study area, which represented approximately 50% of the total catchment area draining to this stream, the remainder consisting of a mixture of arable, woodland, and concrete/grass areas within the Santa Pod raceway to the west of the site.

### **Sampling**

Two monitoring stations were established to measure and sample runoff generated from within the study area, with a further three stations at points where runoff had been identified as entering from outside. These additional positions were designed to quantify this external runoff component, and assess leachate movement in order to obtain nett values for the study area.

The automatic flow recording and sampling system installed at each of the monitoring locations consisted of a Wessex flume and an ultrasonic water depth probe linked to an electronic data capture system based on a Campbell Scientific CR10 datalogger, with data transfer by mobile telephone link. Water samples were collected during drainage events using EPIC automatic wastewater samplers, with flow related sampling controlled by the datalogger program. These systems collected drainage water directly as it either entered or left the study area, providing a sensitive method of monitoring leaching losses to surface waters.

### **Pesticides studied**

Initially, (October 1999 to February 2000) water samples were analysed for a wide range of pesticides in order to determine which substances may be impacting the main stream from outside the study area, and if there had been any "carry over" from pesticide use within the study area in previous years. This analysis suite of pesticides is listed in Table 1.

Table 1. Pesticide analysis suite – October 1999 to February 2000

Acephate	Diflufenican	hosalone
Azinphos-methyl	Tebuconazole	Phosmet
Carbophenothion	Azoxystrobin	Phoshamidon
Chlorfenvinphos	Isoproturon	Pirimiphos-methyl
Chlorpyrifos	MCPA	Pyrazophos
Chlorpyrifos-methyl	MCPB	Quinalphos
Diazinon	Bentazone	Triazophos
Dichlorvos	Parathion-ethyl	Terbutylazine
Dimethoate	Parathion-methyl	Pirimicarb
Ethion	Malathion	Terbutyrn
Etrimfos	Methacrifos	Cyanazine
Fenchlorphos	Methacrifos	Metazochlor
Fenitrothion	Methamidophos	Fluazipop-butyl
Heptenophos	Methidathion	Mevinphos
Omethoate	Monocrotophos	

From March 2000 samples were only analysed for pesticides which had been applied to the study fields, although analytical methods for some of these active substances were not available at the laboratory undertaking the analysis. Pesticides applied to the study area are listed in Table 2.

Table 2. Pesticides applied to the study area from autumn 1999 to January 2001

Active substance	Analysis	Date applied
IPU	Yes	10/3/00
MCPB	Yes	14/5/00
Terbutyrn	Yes	1/4/00
Terbutylazine	Yes	1/4/00
Tebuconazole	Yes	1/4/00
Trinexapac-ethyl	Yes	8/5/00
Bentazone*	Yes	14/5/00
Trifluralin	Yes	10/3/00
Epoxiconazole	Yes	8/5/00
Chlormequat	Yes	8/5/00
Clodinafop-propargyl	No	3/5/00
Metasulfuron-methyl	No	6/5/00
Fluroxypyr	No	6/5/00
Cyanazine	Yes	14/5/00
Kresoxim-methyl	No	20/5/00

## RESULTS

Very few pesticide detections were made during winter 1999-2000, before the majority of pesticides were applied at the site during spring 2000 (Table 2). Of the chemicals listed in Table 1, MCPA/MCPB was detected at low concentrations (maximum  $0.15\mu\text{g L}^{-1}$ ) in drainage entering from outside the study area in late October 2000. Isoproturon was occasionally detected in flow entering from outside the study area in concentrations up to  $0.37\mu\text{g L}^{-1}$  throughout the winter period, although no detections were made at the catchment outlet, suggesting that dilution in the main stream had brought levels to below the detection limit of  $0.05\mu\text{g L}^{-1}$ .

The spring of 2000 was characterised by periods of heavy rainfall, with drainage continuing into the early summer (Figure 1). A number of the pesticides applied to the study fields during this period were detected in runoff at the catchment outlet. These included the conazole fungicide tebuconazole (maximum  $1.3\mu\text{g L}^{-1}$ ), and the herbicides terbuthylazine and terbuthryn ( $0.21\mu\text{g L}^{-1}$  and  $0.91\mu\text{g L}^{-1}$ ), the latter applied to the single field of peas.

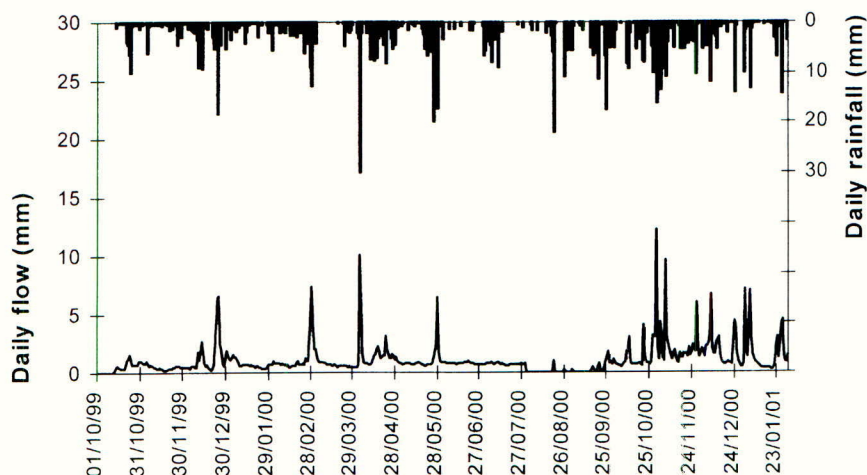


Figure 1 Rainfall and runoff at the catchment outlet – October 1999 to January 2001

The application of the diazinone herbicide bentazone, and the triazine herbicide cyanazine to the pea field in late May (Table 2) occurred towards the end of the drainage season, giving little opportunity for leaching to surface water over the summer when little or no drainage occurred. However, with an early commencement of drainflow in September 2000, as a result of the extremely wet autumn, these two chemicals were detected at the catchment outlet at concentrations of  $6.0$  and  $1.4\mu\text{g L}^{-1}$  respectively, declining to  $0.08$  and  $0.12\mu\text{g L}^{-1}$  by January 2001.

Leaching losses of pesticides from the study area were calculated from the measured concentrations and flow volume from each runoff event, and are presented in Table 3. The

highest estimated pesticide leaching loss was for cyanazine, amounting to 2.0% of the total pesticide applied. With the exception of isoproturon, none of the chemicals monitored at the catchment outlet were detected entering the study area from the wider catchment, therefore it is most likely that the losses reported were a result of pesticides leaching from the study fields only.

Table 3. Pesticide losses – calculated at the catchment outlet

Pesticide (active substance)	Maximum concentration ( $\mu\text{g L}^{-1}$ )	Total loss (g/ha)	% loss of applied
Bentazone	6.0	0.79	1.4
Cyanazine	1.4	0.21	2.0
Terbuthylazine	0.21	2.83	1.3
Tebuconazole	1.3	0.67	0.4
Terbutryn	0.91	5.08	1.0
Isoproturon	0.18	0.15	0.02
Trifluralin	0.15	0.07	0.007

## DISCUSSION

During the first year of this study information on the leaching of pesticides from the arable system was quantified to provide a baseline for the future sustainable management programme. Monitoring of runoff originating from outside the study area confirmed that losses recorded at the catchment outlet could be attributed to pesticide applications made to the study fields, while measurement of runoff volume allowed the accurate estimate of individual pesticide losses.

Several of the pesticides applied during spring 2000 were detected at the catchment outlet soon after application at concentrations above the EC drinking water limit of  $0.1\mu\text{g L}^{-1}$ . The detection of the herbicides terbuthylazine ( $K_{oc}=278$ ) and terbutryn ( $K_{oc}=1089$ ) was significant as they had been applied to a single field of peas, representing only 15% of the total study area. It was probable that concentrations at the field drain would have been greater than the  $0.21\mu\text{g l}^{-1}$  to  $0.91\mu\text{g l}^{-1}$  measured at the catchment outlet when dilution factors were considered. Although these two chemicals may be regarded as having only a moderate leaching potential (Gustafson, 1993), application took place during an unusually wet spring, with extensive drainage occurring soon after application (Table 2, Figure 1). These conditions probably represented a "worst case" in terms of leaching risk (Jones *et al.*, 2000). Total losses of terbuthylazine and terbutryn were influenced by the extensive drainage recorded in April/May 2000, with runoff continuing much longer than the average for this area of the UK (MAFF 1984). The presence of the herbicides bentazone and cyanazine in leachate following the early resumption of drainage in September 2000 was an indication of the relative

2000). Total losses of terbuthylazine and terbutryn were influenced by the extensive drainage recorded in April/May 2000, with runoff continuing much longer than the average for this area of the UK (MAFF 1984). The presence of the herbicides bentazone and cyanazine in leachate following the early resumption of drainage in September 2000 was an indication of the relative persistence of these chemicals (Hollis 1991), in addition to their high leaching potential. The total losses of between 1.4% and 2.0% of active substance applied were again influenced by the extreme weather patterns which characterised this period, with autumn drainage occurring some 4 to 6 weeks in advance of the normal patterns historically observed in this area.

In contrast to the pesticides applied to the pea crop, losses of isoproturon (high leaching potential) applied to the winter wheat crop during March 2000 were much less (0.02% of applied), with no detections from some of the sampled events during the spring period. The reason for this was not apparent, although the relatively dry three week period between application and the first significant drainflow may have been an important factor. Conversely, the conazole fungicide tebuconazole, applied at the beginning of the much wetter month of April, was detected in leachate for the remainder of the drainage season. The triazole fungicide epoxiconazole, with similar leaching characteristics, but applied in drier conditions six weeks later, was not detected in the final spring sampling event at the end of May 2000, perhaps emphasising the complexity of the processes observed at the site, and the importance of the timing of pesticide applications on leaching losses in this monitoring year. The observations reported here are supported by recent results from the pesticide leaching experiment at Brimstone Farm (in preparation), where long-term monitoring results have demonstrated the importance of soil moisture status to the mobility of pesticides including isoproturon in the period immediately following application.

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## A method for a diagnosis of the risk of pesticides transfer at field scale: principles, implementation and first results in Bretagne (Brittany)

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### ABSTRACT

The presence of pesticides in the rivers of Brittany was underlined at the beginning of the nineties. This pollution was found to be persistent, especially for a few herbicides used on grain crops. As the CORPEN (the national committee on water and pesticides) developed a plot scale method to minimise the transfer risk of pesticides in water, the CORPEP (a regional group on water and pesticides) finalised a specific method intended to the watersheds of the « Bretagne Eau Pure » program. The two methods, however, have the same object and scientific basis. The CORPEP method is specific to the region, in relation to its hydrological and geological characteristics, and the large area of its application. It is based on five factors which are taken into account simultaneously to give a final rank to the plot. The ranks are divided into three classes of transfer risk. The principles of the method and the implementation of the diagnosis are described. An evaluation of the method is laid: progress report in Brittany and first results on water quality.

### INTRODUCTION

In Brittany, the monitoring of pesticides in surface water began in 1990. These last ten years, both surfaces of maize and cereals represent around 25 percent of total agricultural surface, and the grasslands around 40 percent (Agreste, La statistique agricole). As a result, the most frequent pesticides found in raw water are atrazine, the major herbicide used on maize, and isoproturon, the major one used on cereals. Frequencies of detection and maximal values since 1990 are presented below for atrazine (Table 1).

Table 1. Atrazine: Monitoring data from the CORPEP rivers network (samplings after a minimum 10mm rainfall event within 24 hours)

Year	Number of water samples	Rate of detection	Rate of concentrations >0,1 µg.L <sup>-1</sup>	Maximum value (µg.L <sup>-1</sup> ) (day/month)
1990	28	93%	79%	6.8 (25/06)
1991	20	80%	70%	3.1 (09/07)
1992	24	88%	83%	14.7 (01/07)
1993	15	100%	100%	14.8 (10/06)
1994	24	88%	79%	11 (18/07)
1995	17	100%	88%	5 (03/07)
1996	63	94%	86%	8.4 (17/05)
1997	51	100%	96%	29 (16/06)
1998	62	94%	81%	4.1 (10/06)
1999	70	93%	66%	6.3 (19/05)
2000	77	94%	60%	11.1 (10/05)

For each year, the frequency of detection is high and the maximum value can reach several micrograms per litre. The pollution of surface waters by pesticides involves specific and expensive treatments to deliver water in accordance with the national regulations.

To minimise the impact of pesticides in water, the choice is made to manage the transfer risk instead of banning some of them. A method is elaborated, consisting in controlling the transfer risk of the most frequent herbicides used on crops and found in water: atrazine and isoproturon.

## **THE DIAGNOSIS AT THE FIELD SCALE**

### **Historic**

The CORPEP method is specifically designed for the hydrological context of Brittany. It is developed at the end of the nineties to decrease the maximum concentrations occurring during a flood, after herbicide applications (Cann, 1995; Gascuel & Molenat, 2000). As a consequence, the method takes into account the rapid water flows in the watershed, which may have an impact on the water quality downstream: surface runoff, superficial water tables, and flows along the sides through drains and ditches.

The CORPEP research indicated that the mobility and the persistence of herbicides on one hand and the field characteristics on the other hand, determine the potential for herbicide pollution (Gillet, Clement *et al.*, 1995). Experiments of the « Service Régional de la Protection des Végétaux » (SRPV) on a small watershed underlined the specific contribution of a few fields to water pollution downstream (Gillet, 1999). Therefore, a method for a diagnosis at the field scale was chosen.

### **The watershed approach**

The method was designed initially for the watersheds of the programme « Bretagne Eau Pure » (1995-1999). Nineteen watersheds (from 2000 to 40000 hectares) were selected in 1995, with a common objective: to restore the water quality towards pesticides and nitrates.

As the CORPEP method is designed for watersheds, unvarying factors at this physical scale are considered not relevant. This is the case for the time separating the treatment and the first rainfall event, and for geology.

As those watersheds cover around 10 percent of the Brittany surface, the scope of the programme requires a method easily implemented by a large number of farming consultants, and a permanent diagnosis (independent of yearly conditions: crop, soil characteristics, weeds development). Nevertheless, the diagnosis is based on field observations. It needs a rigorous and systematic analysis of the water path into the field.

### **The five factors**

Five factors are selected for the diagnosis. They characterise the field topography (within the field, and inside the watershed) and the agricultural and landscape planning at the field scale. The main factors are physical factors. They have an effect on surface runoff (slope and distance to waterway) and subsurface runoff (drains). The other factors are anthropogenic (length of slope, buffer zone at the bottom of the plot). As these last ones can change, they contribute to adjust the physical factors.



For each factor, a criterion and the classes relating to the criterion are selected (Table 2). The classes are established according to the CORPEP's research (Gascuel-Oudoux & Arousseau, 1999).

Table 2. Factors, hierarchy, criterions and classes for the final rank of the field

Factor	Criterion	class
Distance	On the water path, the distance between the downstream point of the field and the hydrographic network.	3 classes: < 20m
	Hydrographic network: waterways (permanent or temporary) and ditches (in circulation at least three months during winter time)	from 20 to 200m > 200m
Slope	On the water path: slope between the upper point and the lower point	3 classes: < 3%
		from 3 to 5%
		> 5%
Drainage	Agricultural drain underground	2 classes: presence / absence
Length of slope	On the water path: distance between the upper point and the lower point	3 classes: < 50m
		from 50 to 150m
		> 150m
Protection downstream	Presence of a continuous and long-lasting protection, avoiding any direct transfer: grassed or wooded buffer strips larger than 20m, hedges	2 classes: presence / absence

### The final rank

The combination of the five factors is based on the SIRIS method, used by the French ministries of environment, of health and of agriculture (Vaillant *et al.*, 1995). The SIRIS method forms into a hierarchy the five factors. The method takes them into account simultaneously to assign a final rank to the field. Ranks range from 0 to 100 and are divided into three classes of transfer risk of pesticides: low, medium or high risk. The higher the rank is, the higher the transfer risk is. Two tables (depending on whether the field is drained or not) enable the farming consultant to determine the class of each criterion. The reading is possible in lines or in columns and leads to the final rank by a process of elimination (Table 3).

Table 3. Determination table for the SIRIS rank of drained fields

	Length of slope	Distance									
		> 200m			20 - 200m			> 20m			
		< 3%	3 - 5%	> 5%	< 3%	3 - 5%	> 5%	< 3%	3 - 5%	> 5%	
With protection	< 50m	6	13	20	22	31	41	38	40	45	
	50 - 150m	9	17	24	27	37	48	46	49	52	
	> 150m	11	20	29	32	43	54	51	58	62	
Without protection	< 50m	9	17	26	30	41	51	47	55	59	
	50 - 150m	12	22	31	36	48	59	55	65	70	
	> 150m	16	26	37	42	55	68	69	84	100	
22	Low risk	22			Medium risk			22			High risk

## IMPLEMENTATION AND USE OF FIELD DIAGNOSIS

### Implementation

The farming consultant is chosen by the farmer and realises the diagnosis with him. Every field is analysed separately. The consultant observes the water path and fills the different classes of criterions using the farmer's information when necessary (drain). At the end of the diagnosis, both of them get a map where the fields appear coloured in green, yellow or red (respectively low, medium or high risk).

### The guidelines for a prevention of risk of water pollution by pesticides

The second step consists in adapting the agricultural practises to limit the diffuse pollution risk by pesticides. In each watershed, a charter signed by the farming consultants and the herbicides suppliers, defines the guidelines to protect water quality from pesticides. The charter gives recommendations to reduce the risk level by agricultural planning (grassed buffer strips, hedges). If the risk level cannot be changed, it can be managed by a combination of mechanical and chemical weeding or an exclusively mechanical weeding, and by substituting molecules with a more favourable environmental profile for worse environmental behaviour molecules.

As atrazine and isoproturon are the most frequent pollutants found in water, substitution recommendations focus on those two herbicides. The aim is to choose molecules according to the risk level of the field (Table 4). Therefore, molecules are classified into three groups according to their rate, their mobility ( $K_{OC}$ ) and their persistence ( $DT_{50}$ ). The first group gathers herbicides which have a low potential for mobility; the second group, herbicides with low persistence but with a high potential for mobility; and the third group, the herbicides with high persistence and mobility.

Table 4. Correspondence between groups of herbicides and risk levels of fields

	Risk level		
	Low risk	Medium risk	High risk
Group 1	Yes	Yes	Yes
Group 2	Yes	Yes	No
Group 3	Yes	No	No

For example, alachlore belongs to the third group; it can be applied only on low risk fields. This filling is based on physical and chemical properties of herbicides, but is corrected every year according to the monitoring data by a CORPEP commission. Monitoring data come from a regional « surveillance network » of water quality and from every « Bretagne Eau Pure » watershed.

## RESULTS AND DISCUSSION

A specific test of the charter guidelines is conducted in 2000 on one of the « Bretagne Eau Pure » watershed. On a small surface watershed (lower than 50 ha), the farming consultants and the farmers are supplied with a financial aid. The complete respect of the charter is required to get the subsidy (it is not the case in the other watersheds).

The test demonstrates that, if the charter is respected, it is possible to control the water pollution by maize herbicides.

From 1999 to 2000, maize surfaces increased on this watershed from 15 to 23 hectares. It is still possible to apply atrazine on more than 10 hectares (instead of less than 6 hectares in 1999). In spite of that, atrazine concentrations in water remain under  $0,22\mu\text{g.L}^{-1}$  in 2000 (Figure 1), which means more than six times lower than the 1999 maximum concentrations. At the exit of the entire watershed, the monitoring reveals that none of the other maize herbicides used are found in the water at upper concentrations than  $0,1\mu\text{g/l}$ .

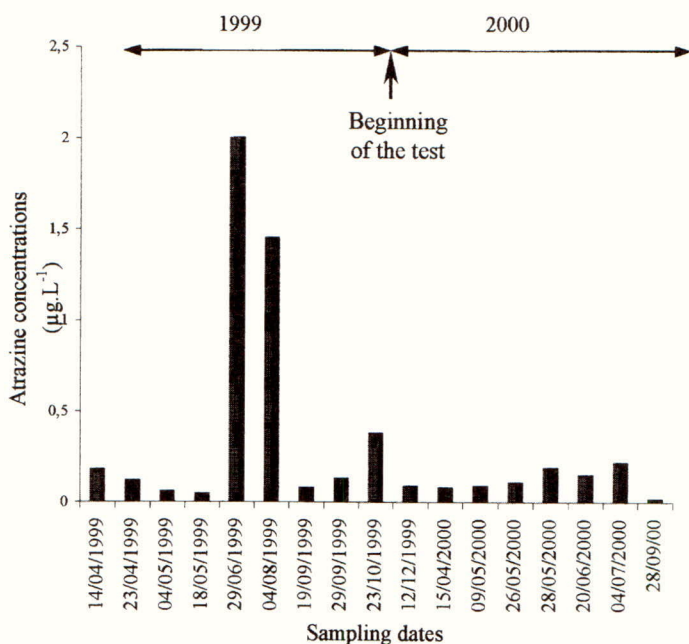


Figure 1 Atrazine concentrations in water downstream the small watershed. (Samplings in water after a minimum 10mm rainfall event within 24 hours)

These first results are confirmed in a few watersheds of the « Bretagne Eau Pure » programme, where water quality regarding atrazine is improving. On those watersheds, both frequencies of concentrations above  $0,1\mu\text{g.L}^{-1}$  and maximum concentrations of atrazine are decreasing. The same results are still expected for isoproturon.

## CONCLUSION AND PROSPECTS

The test indicates, at the scale of a watershed, that it is possible to reduce the atrazine pollution in surface water by adapting the use of pesticides according to the specific transfer risk of the field. It also indicates that the pollution control requires a complete respect of the charter by all the farming consultants and all the farmers of the watershed. For a complete validation of the substitution process, a rigorous monitoring of water is absolutely necessary. It is a security, especially regarding to the molecules used for substitution. Today (beginning of 2001), 300 consultants are trained to implement the CORPEP method and the transfer risk diagnosis concerns more than 30000 hectares. The method will probably develop in the Brittany Region: with the « Bretagne Eau Pure » 2000-2006 programme concerning around

40 percent of the Brittany region, and with the new dispositions developed by the French ministry of agriculture to promote sustainable agriculture. In the rest of France, diagnosis of the transfer risk of pesticides at the field scale are also developing. They are based on the CORPEN method which implies an agronomic section but can be applied everywhere. Like in Brittany, they are designed for watersheds selected for their contribution to pollution.

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