

Characterisation of the structure of spatial variability for initial pesticide concentration in a field trial

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ABSTRACT

The spatial variation in the concentration of four herbicides in two trials with maize (metolachlor, terbutylazine) and winter wheat (pendimethalin, isoproturon) was assessed during the treatment, using classical statistical and geostatistical techniques. Spray trap and soil samples were collected immediately after the treatment to evaluate the herbicide concentration when the solution reaches the soil and the initial herbicide soil concentration, respectively. The results show that the values of the herbicide concentration at the moment of treatment are lower than expected, indicating that under field conditions only a part of the pesticide reaches the soil during the distribution. A decrease of CV in spray traps in winter wheat trials is partially explainable by the greater accuracy used in treatment planning and the better weather conditions. Geostatistical analysis was undertaken on the herbicide concentration in the spray traps, as 80 samples per herbicide were collected, while there were not enough samples for initial soil concentration to perform this kind of analysis. The data showed a spatial correlation only for maize herbicides. The data are discussed in order to establish a more efficient soil sampling strategy.

INTRODUCTION

One of the main problems in field studies of pesticide dissipation is the high variability in pesticide application (Wauchope *et al.*, 1977; Vischetti *et al.*, 1997). The application of pesticides under normal farming conditions is often done with little attention to the factors which can generate spatial variability in the pesticide concentration. In many field experiments carried out following standard farming practices, without any kind of interference, high variability in the initial distribution of pesticides has been found (Vischetti *et al.*, 1995; Vischetti *et al.*, 1998). Among other factors, uneven soil preparation, wind speed at the time of treatment, irregular speed of the spraying equipment and changing pressure at the nozzles, determine spatial variability in pesticide distribution. Together with the high variability, the loss of pesticides at the moment of treatment almost always happens in field experiments on pesticide fate. The loss can be high and not only explainable with the action of some factors such as wind speed or low recoveries of pesticides from soil samples (Vischetti *et al.*, 1998).

Geostatistics is a technique used to determine the spatial variability of some soil properties such as organic matter content and texture (Webster & Burgess, 1980; Vieira *et al.*, 1981), but this technique has only been used in a few cases to characterise the spatial variability of pesticide concentration in fields (Rao & Wagenet, 1985; Vischetti *et al.*, 1997). A possible use of geostatistics is to characterise the structure of the spatial variability in order to establish an experimental design for further trials on pesticide dissipation studies, namely the number of samples that should be taken depending on the variability and field size.

The first aim of this study was to assess the spatial variation in the concentration of four herbicides under field conditions; the second was to compare the herbicide soil concentration (initial concentration) with the herbicide concentration in glass spray traps before the solution reaches the soil.

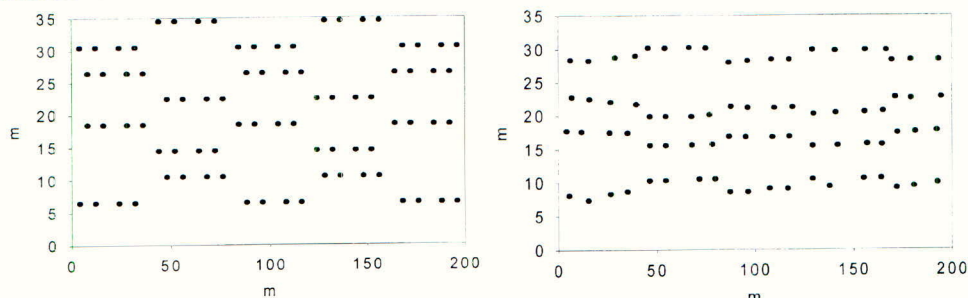


Figure 1. Arrangement of spray traps in maize (left) and in winter wheat (right)

MATERIALS AND METHODS

Field study

Table 1. Field information

| | | Soil properties | | | | | | |
|---------------------------------------------------|---------------------------------|-----------------|------------------|-------|----------------|-----------------|--------------------------------------|-------|
| Depth | pH | Organic Matter | Clay | Silt | Sand | CEC | | |
| 0-50 cm | 8.11 | 0.92% | 11.8% | 44.9% | 43.3% | 12.87 meq/100 g | | |
| Weather conditions during herbicide application * | | | | | | | | |
| | Wind speed (m s ⁻¹) | | Air humidity (%) | | Temperature °C | | Sun radiation (W h m ⁻²) | |
| | maize | wheat | maize | wheat | maize | wheat | maize | wheat |
| Mean | 0.7 | 2.1 | 65.3 | 85.2 | 21.5 | 15.0 | 492.1 | 236.1 |
| Min | 0.2 | 0.8 | 61.0 | 75.0 | 20.6 | 13.0 | 209.3 | 62.8 |
| Max | 1.2 | 3.5 | 75.0 | 98.0 | 22.5 | 16.8 | 676.8 | 425.6 |

* The application duration was 30 minutes

The study was done during 2000 on the Padova University Experimental Farm (45°12' N, 11°58' E) in north-eastern Italy. The experimental field (200 x 31.5 m) was cropped with maize and winter wheat, following standard agronomic practices. The herbicides used were metolachlor (M) and terbuthylazine (T) in maize; isoproturon (I) and pendimethalin (P) in winter wheat; the herbicides were applied 28/10/2000 (maize) and 27/10/2000 (winter wheat) as tank and ready-mix in the two crops, respectively, at the following rates: M 2200 g a.s. ha⁻¹

and T 1100 g a.s. ha⁻¹, I 900 g a.s. ha⁻¹ and P 950 g a.s. ha⁻¹. Herbicides were applied using a tractor-mounted Hardy LY-HY sprayer equipped with a 16 m boom and 4110-16 fan nozzles. Before spraying, 80 spray traps of 113 cm² with a filter paper at the bottom were placed on the soil surface to determine herbicide concentration when the solution reaches the soil. A map of the traps is shown in Figure 1: trap layout consisted of eight rows, four for each sprayer pass, along the longer field axis. Within 5 minutes of application, the traps were covered and stored at 4°C until analysis. After spraying (1-2 h), soil samples were taken to assess concentration of herbicide in soil: 20 soil samples were collected in maize, eight in winter wheat at a depth of 0-5 cm. Soil properties and weather conditions during the trials are given in Table 1.

Herbicide extraction and analysis

Spray trap samples were washed with methanol and soil samples with 100 mL of a 50/50 methanol/water mixture. The analysis of M, T and P was performed by gas chromatography while the analysis of I was performed by HPLC. The retention times were 14.1 min for M, 12.2 min for T and 15.5 min for P, and the sensitivity was 1 µg kg⁻¹ for T and P and 2 µg kg⁻¹ for M. The retention time for I was 10.5 min and the sensitivity was 8 µg kg⁻¹.

Geostatistical analysis

The GS+ Program (Gamma Design Software, 1992) was used for geostatistical analysis. The program calculates the semivariance $\gamma(h)$ as follows:

$$\gamma(h) = 1 / [2N(h)] \cdot \sum_{i=1}^N [z(i) - z(i+h)]^2$$

where $N(h)$ is the number of pairs $z(i)$, $z(i+h)$ of samples that are separated by a lag distance of h . A plot of γ versus h is called a semivariogram. Although, by definition, $\gamma(h) = 0$ when $h = 0$, it is often found in practice that as h approaches 0, $\gamma(h)$ approaches a positive finite value, which is commonly called the nugget effect, C_0 . As h increases, $\gamma(h)$ often increases up to some value, say a , after which it remains approximately constant. The plateau value of $\gamma(h)$ at this point, referred to as the sill C , is equal to the total variance of the data and the distance a is called the range and represents the separation distance beyond which the parameter values are unrelated, that is, spatially independent. When the semivariogram shows complete discontinuity at the origin, then $\gamma(h) = C$ and there is a pure nugget effect.

RESULTS AND DISCUSSION

The range of the herbicide concentration (CV) in spray traps was between 9.5 and 31.3%; the high values of CV for M and T are in agreement with other reports of field experiments in farming scenarios. The CV for I and P was 9.5% and 17.7% respectively, which was much lower than those found for other pesticides in real farming conditions (Walker & Brown, 1983; Vischetti *et al.*, 1998). This low variability is partially explainable by the accuracy used in planning the treatment and the more favourable weather conditions: the soil was well prepared in order to have an even seed bed and the herbicides were distributed with great attention, controlling the speed of the tractor, the pressure of the nozzles and the boom oscillations. The higher relative air humidity and the lower temperatures contributed towards

reducing the vaporisation losses between the herbicide application and the closing and collecting of the traps. The wind speed during the application was very low in both experiments, particularly the first, so this variable does not seem to have influenced the application uniformity.

Table 2. Mean concentration for application rate and initial soil concentration for the four herbicides and relative statistical parameters

| Application Rate | Terbuthylazine | Metolachlor | Pendimethalin | Isoproturon |
|-----------------------------------|----------------|--------------|---------------|-------------|
| Number of samples | 80 | 80 | 80 | 80 |
| Mean (g ha ⁻¹) ± s.d. | 481.0±150.6 | 2202.6±682.4 | 466.0±82.8 | 576.6±54.8 |
| Min (g ha ⁻¹) | 145.7 | 522.4 | 309.9 | 470.8 |
| Max (g ha ⁻¹) | 818.7 | 3765.4 | 628.3 | 679.3 |
| C.V. (%) | 31.3 | 30.9 | 17.7 | 9.5 |
| Initial soil concentration | | | | |
| Number of samples | 20 | 20 | 8 | 8 |
| Mean (g ha ⁻¹) ± s.d. | 285.4±105.1 | 654.8±193.5 | 189.9±114.8 | 648.7±378.5 |
| Min (g ha ⁻¹) | 132.8 | 624.5 | 62.3 | 304.4 |
| Max (g ha ⁻¹) | 511.5 | 1015.3 | 395.3 | 1499.6 |
| C.V. (%) | 36.8 | 29.5 | 60.5 | 58.3 |

The mean values of both herbicide concentration in the spray traps and initial soil concentration were lower than expected. The differences could be ascribed to the fact that at the end of the treatment the sprayer might still contain some pesticide in the distribution circuit. This was not checked in the experiment. The initial soil concentration of the four herbicides in the two experiments was lower than the application rate and this can mainly be ascribed to the extraction and handling of the soil samples and to the analytical method that allowed recoveries lower than 100% and led to an initial concentration value lower than that determined in the spray traps where the recoveries were always around 100%. According to Otto *et al.*, (1998), the volatilisation processes may be divided into two phases with very different loss rates. During the first phase, before reaching a partition equilibrium in the soil, volatilisation rates are very high, reaching in a similar environment, levels of about 10% of the amount in the soil per day for terbuthylazine. The delay in soil sampling could at least partially explain the discrepancy between the herbicide concentration in the traps and the soil. Geostatistical analysis was undertaken on the herbicide concentration in the spray traps where 80 samples per herbicide were collected, while the samples for initial soil concentration were not sufficient to perform this kind of analysis. Data from the geostatistical analysis showed a spatial correlation for maize herbicides (M and T) and provided the sill, nugget and range values, while the data for wheat herbicides (I and P) showed a pure nugget effect, namely a lack of structure of variability (Figure 2). Geostatistical parameters for M and T are reported in Table 3. The spherical model described the data variability well in both cases with $p < 0.01$. The sill values were similar to the total variance of the experiment and that of M was noticeably higher. The nugget effect was about 40% of the total variance for both herbicides, thus indicating a variability in the samples coming from sites quite close to one another. The range was 37.6 m for M and 40.1 m for T and this indicates that the variability remains constant over these distances. The wheat herbicides showed semivariograms with a complete discontinuity at the origin, with a pure nugget effect that corresponds to a total lack of structure of variability. In this case variability

is present from point to point and there is an absence of spatial correlation, at least at the sampling scale used. The sill is very low in both cases and indicates the accuracy in preparing the experiment.

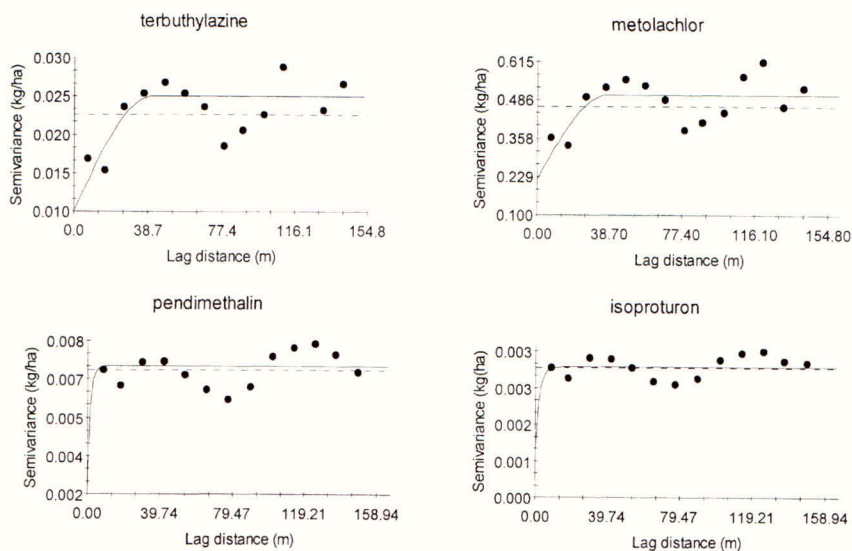


Figure 2. Semivariograms for herbicide concentrations in boxes.

Table 3. Geostatistical parameters for maize herbicides

| Isotropic | | | | | |
|-------------------|-----------|--------|-------|-------|-------|
| | Model | Nugget | Sill | Range | r^2 |
| Metolachlor | spherical | 0.217 | 0.503 | 37.20 | 0.405 |
| Terbutylazine | spherical | 0.010 | 0.025 | 40.90 | 0.418 |
| Anisotropic | | | | | |
| | Model | Nugget | Sill | Range | r^2 |
| Metolachlor 0° | linear | 0.378 | 1.134 | 696 | 0.431 |
| Metolachlor 90° | linear | 0.303 | 1.057 | 241 | 0.431 |
| Terbutylazine 0° | linear | 0.017 | 0.054 | 536 | 0.436 |
| Terbutylazine 90° | linear | 0.015 | 0.051 | 241 | 0.436 |

Analysis of the anisotropic semivariograms allows the effect of the treatment application on the data variability to be considered. The semivariograms at 0 degrees were performed with the vector only in the direction of the x-axis and indicate the variability between the rows where the spray traps were positioned. The semivariograms at 90 degrees were performed with a vector perpendicular to the x-axis and indicate the variability within the row. The semivariograms for maize herbicides are reported in Figure 3. The increase of variability in the semivariograms indicated that the mode of treatment strongly influences the variability in herbicide concentration. The 0 degrees variograms presented only three points because the number of traps was insufficient for a larger number of points, and the steep slope indicates a large increase in variability between rows. Under these conditions it is quite impossible to define a range. The 90 degrees variograms also showed an increasing of variability but lower

than that at 0 degrees. In all cases the linear model describes the trend well, indicating that under the experimental conditions, the sampling strategy was not sufficient to estimate a range; in particular along the axis perpendicular to the main field one, the number of traps was insufficient to estimate spatial variability.

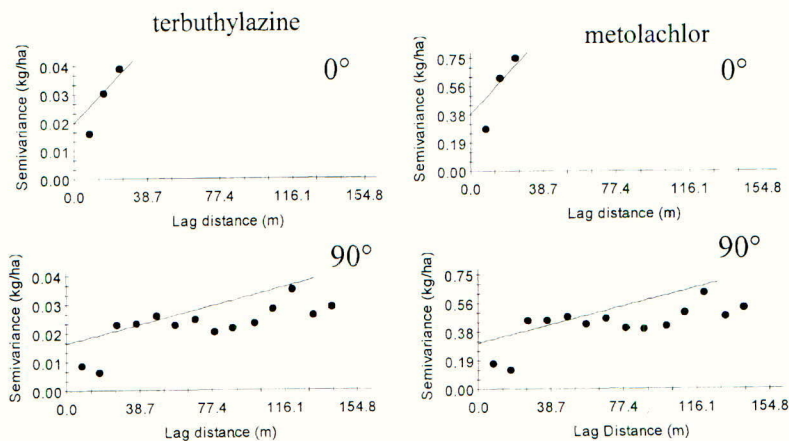


Figure 3. Anisotropic semivariograms (0° and 90°) for metolachlor and terbuthylazine

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Predicting atrazine transport into subsurface tile-drained soil using the HYDRUS-2D model : lysimeter study

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ABSTRACT

This study was made to compare the measured with the predicted transport of atrazine into subsurface tile-drained soil through lysimeters using the HYDRUS-2D model. The HYDRUS-2D model was able to predict atrazine movement through the soil profile. The results obtained demonstrate the ability of computer simulation models to predict the potential for groundwater pollution. Thus, we can modify our agricultural management practices to reduce contamination.

INTRODUCTION

Tile drains are commonly used in many agricultural fields to remove excess water from the vadose zone, to maintain optimum soil water contents for crop production, and to maintain a low level of soil salinity or sodicity. Likewise, tile drains have been used to study field-scale transport of solutes (Hallberg *et al.*, 1986). Nitrate or pesticide leaching losses from soils have been evaluated using many methods such as tile drains (Bergstrom, 1987), pan lysimeters (Fermanich *et al.*, 1991), monolith lysimeters (Owens, 1987) and soil columns (Allepalli & Govindaraju, 1994).

Increasing concern over pesticides in surface and ground water has required the evaluation of their mobility as a basis of risk analysis. Lysimeters offer good possibilities to conduct such tests, because they constitute closed systems, and they permit control of water movement through the soil (Bergstrom, 1990; Hance & Fuhr, 1992). Drainage lysimeters, both with and without tension, have been used to study agrochemical leaching and water movement (Tyler & Thomas, 1977; Bergstrom, 1990; Bergstrom & Johansson, 1991).

The objectives of the present study were: 1) measuring atrazine transport in tile-drained soil lysimeters, 2) evaluating the HYDRUS-2D model for predicting atrazine transport in the lysimeter systems; and 3) comparing observed versus simulated data for atrazine transport.

MATERIALS AND METHODS

Soils

Three types of soils were used in the present study, namely, clay loam (CL), sandy clay loam (SCL), and sandy loam (SL). Some properties of the soils are given in Table 1.

Table 1. Soil properties

| Soils | Particle size distribution, % | | | ρ_b Mg m ⁻³ | O.M. % |
|-----------------|-------------------------------|------|------|--------------------------------|-----------|
| | sand | silt | clay | | |
| Clay loam | 41 | 20 | 39 | 1.27 | 1.8 |
| Sandy clay loam | 46 | 27 | 27 | 1.35 | 0.5 |
| Sandy loam | 55 | 33 | 12 | 1.48 | 1.2 |

Herbicide

Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) was selected for the present study. It has a water solubility of 33 mg L⁻¹ and half-life of 64 days (Singh *et al.*, 1990).

Lysimeters

PVC columns 70 cm long and 15 cm in diameter with closed bottoms were used. The base of the lysimeters was tightly sealed with silicone adhesive. The bottom 5 cm layer in the columns comprised coarse gravel (drainage layer). A perforated plastic tube of 2.5 cm diameter was fitted into the drainage layer to collect the drainage water. The lysimeters were hand-packed with air-dried soil to the desired bulk density by gently tapping. The subsurface-tile drain was fitted at 60 cm below the soil surface.

Water and atrazine application

Water was added to the soil until steady-state water flow conditions were established. Each lysimeter unit was connected to a suction pump and subjected to -340 cm water tension (-33 kPa; field capacity condition). Atrazine was applied at a rate of 50 $\mu\text{g cm}^{-3}$ using CaCl₂ (0.001 M) as a background solution at 2.0 cm d⁻¹ with a pulse period of 1 day. Water flow then continued for 100 days at a constant rate of 2.0 cm d⁻¹. The suction heads (h) in the lysimeter soils were monitored periodically during the application period using small mercury tensiometers located at 5, 10, 15, 20, 40 and 60 cm below the soil surface. Lysimeters were monitored daily for drainage. Collected drainage water was weighed and expressed as volume per surface area of the lysimeter.

Extraction and analysis of atrazine

At the end of the experiment, soil samples were collected from the lysimeters at above-mentioned soil depths for atrazine analysis. Samples were extracted three times (3 x 20 ml) using analytical grade hexane. The extract was filtered and atrazine was analyzed by gas chromatography. Samples of drainage water were also analyzed for atrazine at different periods. Atrazine concentration was expressed as $\mu\text{g cm}^{-3}$.

Soil hydraulic parameters

The hydraulic properties of soils were described by Mualem-van Genuchten parameters (Mualem, 1976; van Genuchten, 1980) and are given in Table 2.

Table 2. Parameters of hydraulic functions used in the numerical simulation

| Soils | θ_r $\text{cm}^3 \text{cm}^{-3}$ | θ_s $\text{cm}^3 \text{cm}^{-3}$ | α cm^{-1} | n | K_s | ι |
|-----------------|--------------------------------------------|--------------------------------------------|------------------------------|--------|-------|---------|
| Clay loam | 0.0797 | 0.4429 | 0.01941 | 0.2451 | 11.8 | 0.5 |
| Sandy clay loam | 0.0560 | 0.4777 | 0.02864 | 1.1100 | 21.2 | 0.5 |
| Sandy loam | 0.0641 | 0.4010 | 0.01320 | 1.4445 | 36.2 | 0.5 |

θ_r = soil water content, θ_s = saturation soil water content, α and n = shape parameters
 K_s = saturated hydraulic conductivity (LT^{-1}), ι = pore connectivity parameter (Mualem, 1976)

Solute transport parameters

For atrazine, the transport parameters were taken from the literature (Nicholls, 1994; Allepalli *et al.*, 1994) as shown in Table 3, assuming a linear chemical non-equilibrium reaction and a linear Freundlich adsorption isotherm.

Table 3. Atrazine transport parameters used in the simulation

| Parameters | Symbol | Units | Values |
|--------------------------------------------------------------|---------|-----------------------------|---------|
| Longitudinal pore scale dispersivity | D_L | cm | 0.5 |
| Transverse pore scale dispersivity | D_T | cm | 0.1 |
| Ionic or molecular diffusion coefficient in free water | D_w | $\text{cm}^2 \text{d}^{-1}$ | 1.2 |
| Adsorption isotherm coefficient | β | - | 1 |
| First order rate constant for degradation in dissolved phase | μ_w | d^{-1} | 0.02 |
| Henry's constant | | d^{-1} | 1.3E-07 |
| Pulse time | t_p | d | 1 |
| Applied concentration | C_0 | μg | 50 |
| Steady state water flux | q | cm d^{-1} | 2 |

Modelling

The HYDRUS-2D numerical model (Simunek *et al.*, 1999) was used to simulate water flow and atrazine transport in the different soils and the predicted data were compared with those observed.

RESULTS AND DISCUSSION

Figure 1 shows the observed values of atrazine flux at the drain boundary of the three soils. The data show that the timing of the peak flux differed according to soil texture. The sandy clay loam soil reached a maximum flux at 30 days after application, followed by the sandy loam soil at 45 days, then the clay loam soil at 60 days. The maximum value of atrazine flux ($0.56 \mu\text{g cm}^3 \text{d}^{-1}$) was attained with the sandy clay loam soil, followed by the sandy loam soil ($0.31 \mu\text{g cm}^3 \text{d}^{-1}$), then the clay loam soil ($0.27 \mu\text{g cm}^3 \text{d}^{-1}$).

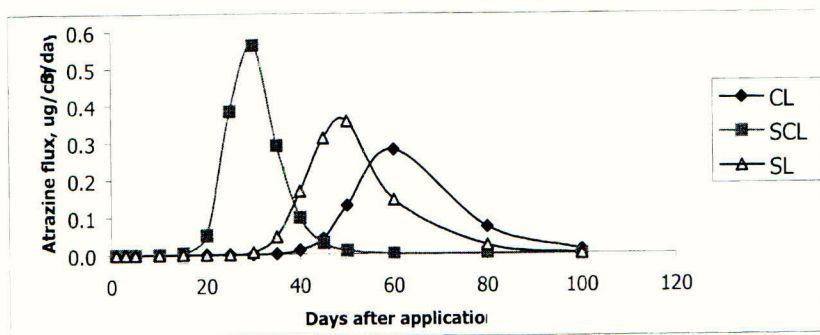


Figure 1. Observed atrazine flux at the drain boundary in the three soils.

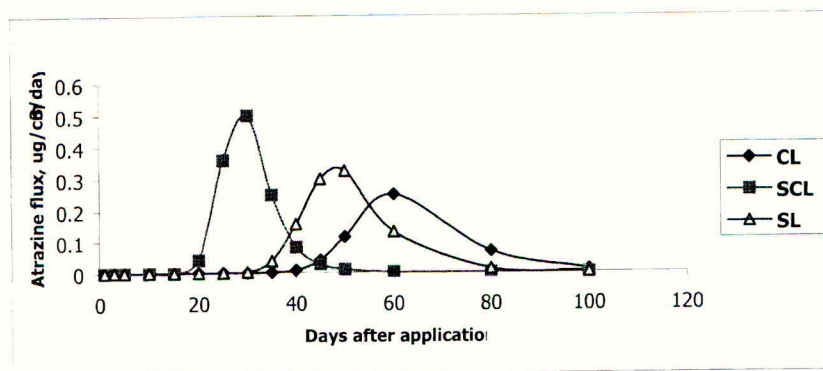


Figure 2. HYDRUS-2D simulations of atrazine flux at the drain boundary in the three soils.

The observed values were, generally, greater than those predicted (Figure 2), but the differences were small. Macropore flow may be an important reason for the differences (Hoffmann & Johansson, 1999). These differences may be attributed to the pore size distribution. At pore-scale, the variations of water and solute flux may be due to the different velocities of water and solute as a result of pore groups in soil. This is an important factor in structured soils with different pore groups, in which bypassing or preferential flow of water and solute transport can occur (Dyson & White, 1987).

Thus, the HYDRUS-2D model successfully predicted atrazine leaching in these experiments (r-values between observed and predicted data ranged between 0.96 and 0.99). The differences among the three soil textures tested may be attributed to their structures, partition coefficients (k_d), and organic matter contents (OM). The arrival times for atrazine transport to tile drains were about 15, 30 and 30 days after application for sandy clay, sandy clay loam and clay loam soils, respectively, under the conditions of these experiments. The differences in local advection velocity of atrazine transport may be attributed to the spatial variability of macropore soil hydraulic properties (Bowman & Rice, 1986; Abdel-Nasser, 2000).

The present experiment technique is useful for assessing relative behaviour of atrazine in different soils, but may not be suitable for describing chemical transport in the field scale soil profile, since it does not account for many chemical processes occurring under natural field conditions.

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Pesticide trends in raw and treated drinking water

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ABSTRACT

Since 1990 when the water industry in England and Wales was privatised, water companies have invested around £1 billion to remove pesticides from sources of drinking water. New treatment processes have produced a substantial reduction in the number of drinking water samples exceeding the national and European pesticide standard of 0.1µg/litre. Local voluntary action by users, stewardship activity by the agrochemical industry and intervention by regulators have also played a part. Understanding the success of these measures requires the analysis of raw water sources, often over long periods. This paper draws together pesticide monitoring data collected by Thames Water over the past 10 years and examines trends over time. In some cases measures to protect drinking water sources have produced clear improvements. In other cases regulatory action is needed to deal with contamination that other approaches have failed to address.

INTRODUCTION

The Water Supply (Water Quality) Regulations 1989 (Anon. 1989) formalised the arrangements for monitoring and reporting the quality of drinking water in England and Wales. The Regulations incorporated the standards required by the European Drinking Water Directive 80/778/EEC and included the standards for individual and total pesticides of 0.1µg/litre and 0.5µg/litre respectively. These two standards were retained in a recent revision of the European Directive (Council Directive 98/83/EC).

In the Thames Water area approximately 75% of the drinking water that is supplied to customers is derived from the river Thames and its tributaries. The remaining 25% comes from groundwater sources. Intensive agriculture, urban development and highways mean that pesticides are widely used in water catchment areas. Contamination of rivers and groundwater by agricultural and non-agricultural pesticides is commonplace. As a result of this, Thames Water has long had a problem with failures of the pesticide standards in treated water (Table 1).

Table 1. Contraventions of drinking water quality standards in the Thames Water supply area during the period 1992 to 2000

| Year | Total number of contraventions - all parameters | Percentage of contraventions due to failure of the pesticide standards (%) |
|------|-------------------------------------------------|----------------------------------------------------------------------------|
| 1992 | 27,532 | 93.8 |
| 1994 | 9,141 | 84.9 |
| 1996 | 1,939 | 36.1 |
| 1998 | 602 | 2 |
| 2000 | 405 | 0 |

Much of the improvement in pesticide compliance is due to the installation of new treatment technologies, such as ozone and granular activated carbon, to break down and adsorb the pesticides that are not removed by conventional treatment processes. Installing these new processes was expensive, costing £10 million or more for a single treatment works. Today the majority of these schemes have been completed, however, the operational and environmental cost of removing pesticides continues: production of ozone and the periodic regeneration of granular activated carbon consume a lot of energy and increase the amount of carbon dioxide produced by the water industry, when other industries are reducing emissions.

The other approach to improving compliance with the drinking water pesticide standard has been to work with a variety of different organisations to minimise pesticide contamination of raw water sources. This approach is consistent with the 'polluter pays principle' and is essential where water treatment works do not have equipment to remove pesticides. Even where such facilities exist they cannot guarantee compliance. The physical and chemical properties of some pesticides may make them less amenable to treatment and spikes of pesticides can overwhelm plant designed to deal with lower levels. These facts have provided common ground for the water and agrochemical industries, often in conjunction with the users of pesticides, to support each other on several initiatives to minimise the impact of pesticides on water quality (White & Pinkstone, 1993, Davies *et al.*, 1993, Court *et al.*, 1995, White *et al.*, 1997).

This paper considers four pesticides that are among the most problematic for Thames Water in respect of complying with the drinking water standard. These pesticides are all weed-killers (herbicides) and have uses within the agricultural and/or the amenity and industrial sectors.

ATRAZINE AND SIMAZINE

In the early 1990s the majority of pesticide failures of the drinking water standard in the Thames Water region were attributable to atrazine and simazine. As traditional methods of water treatment are unable to remove pesticides, the levels measured in drinking water were indicative of those in the raw water. In Figure 1 the atrazine and simazine concentrations in the final water of a treatment works that abstracts from the river Thames are shown. Treatment that could remove both pesticides was installed in 1995. However concentrations of pesticides were already decreasing. This can be explained by the banning of atrazine and simazine for weed control on roads, railway lines and similar industrial/amenity uses. In May 1992 it was announced that from September 1993 the approval for the non-agricultural usage of atrazine and simazine would be revoked 'to reduce residues in drinking water' (MAFF/HSE, 1992).

Following the installation of pesticide removal technology it became more important to monitor the raw water sources themselves in order to identify and understand trends in pesticide concentrations. Monitoring of the Thames has shown that although concentrations of atrazine and simazine generally declined following the non-agricultural ban, both herbicides are still regularly detected at concentrations above 0.1 µg/litre (Figure 2). This suggests that ongoing uses in agriculture, forestry and perhaps, home garden sectors, continue to contaminate water sources. Increased use of atrazine on maize, and applications of simazine in formulated products applied to winter wheat and barley, may explain the seasonal peaks seen in the Thames. Atrazine and simazine have also been found in groundwaters. At one groundwater source, remote from (historical) non-agricultural sources, but located close to

farmland where maize has been grown, atrazine levels in the raw water initially decreased, only to increase again as crops were rotated (Figure 3). Groundwaters can take years to recover from contamination by pesticides, as is shown in Figure 4. This groundwater is situated in a rural area, but a railway line adjacent to the borehole was suspected as the source of atrazine contamination. In order to protect this borehole from contamination an agreement was reached with British Rail (and has continued with Railtrack) whereby atrazine, and latterly diuron, were not to be used on the stretch of railway line close to this groundwater source. As a consequence of this and the non-agricultural ban, levels of atrazine at this site have slowly declined, falling below the drinking water standard in 1999.

DIURON

In anticipation of and following the non-agricultural ban of atrazine and simazine, a number of amenity and industrial users of pesticides switched to diuron. As diuron is poorly adsorbed onto hard surfaces this produced an immediate impact on concentrations of diuron in surface water sources. Fig 5 shows the concentration of diuron measured in the Thames at a raw water abstraction point to the west of London. Co-operation between water companies, the agrochemical companies and users of non-agricultural pesticides has, in general, ensured that concentrations of diuron did not reach the levels of atrazine and simazine seen in the early 90's. Concentrations of diuron in the Thames are regularly greater than 0.1µg/litre between May and September. Further work is needed to reduce amounts reaching water. The annual mass of diuron (concentration multiplied by river flow) at the West London abstraction points has remained at around 120kg. This is equivalent to 2-5% of the total amount used in the upstream catchment. With a fixed input the diuron concentration is largely dictated by river flow. Diuron also poses a threat to groundwater but early working with Railtrack to protect vulnerable sources close to railway line appears to have, in general prevented a rising trend in diuron in groundwaters as concentrations of atrazine have fallen (see Figure 4). That said diuron is now regularly detected, at below 0.1µg/litre, in a few groundwaters in urban areas. This suggests that action to reduce use on roads and pavements is needed in these catchments. The introduction of residual acting pesticides that are less mobile than diuron would be one way forward.

ISOPROTURON

Isoproturon (IPU) is the most problematic agricultural pesticide in the Thames Water area with concentrations at abstraction points routinely exceeding 0.1µg/litre during December to April. Despite considerable stewardship activity by the agrochemical industry and further restrictions on application rates and timing the amounts of IPU reaching the river Thames has not decreased (Table 2).

Table 2. Summary of data relating to the monitoring of isoproturon in the river Thames

| Crop Year* | Total river flow (x10 ¹² litres) | Total mass of IPU (kg) | Number of days exceeding the 0.1µg/litre standard |
|------------|------------------------------------------------|------------------------|------------------------------------------------------|
| 1996/97 | 0.4 | 39 | 46 |
| 1997/98 | 1.2 | 305 | 113 |
| 1998/99 | 1.9 | 423 | 140 |
| 1999/00 | 1.7 | 885 | 161 |
| 2000/01 | 3.4 | 612 | 149 |

* For these calculations the term crop year refers to the period 1 October to 11 May.

The total mass of IPU that reaches the Thames does vary from year to year, but appears to be very dependent on the weather. For example, in the 1996/97 cropping year when relatively little IPU reached the Thames, the weather was particularly dry, which is reflected in the low value for the total river flow. However, in wetter years, particularly when the rainfall occurs in late autumn after IPU has been applied, much larger amounts of IPU are detected in the Thames and there are many more days when the drinking water standard is exceeded.

Whilst the stewardship activity has led to a greater understanding of how pesticides might reach water e.g. from filling and washing sprayers (Aventis, 2000), voluntary actions, changes to recommended rates and new rules on when IPU can be applied have not protected water sources. It would appear that the only way to produce a substantial reduction in the amounts of IPU reaching water sources, in both wet and dry years, would be a significant, >90%, decrease in IPU usage.

CONCLUSIONS

The contamination of drinking water sources by agricultural and non-agricultural pesticides continues to be a problem in some areas. For certain pesticides the establishment of protection zones close to the water source has proved sufficient to reduce pesticide contamination. However, pesticides which are soluble, mobile, applied in large quantities within the catchment and used by many within a short time-frame will require stronger measures if concentrations in drinking water sources are to be reduced.

ACKNOWLEDGEMENTS

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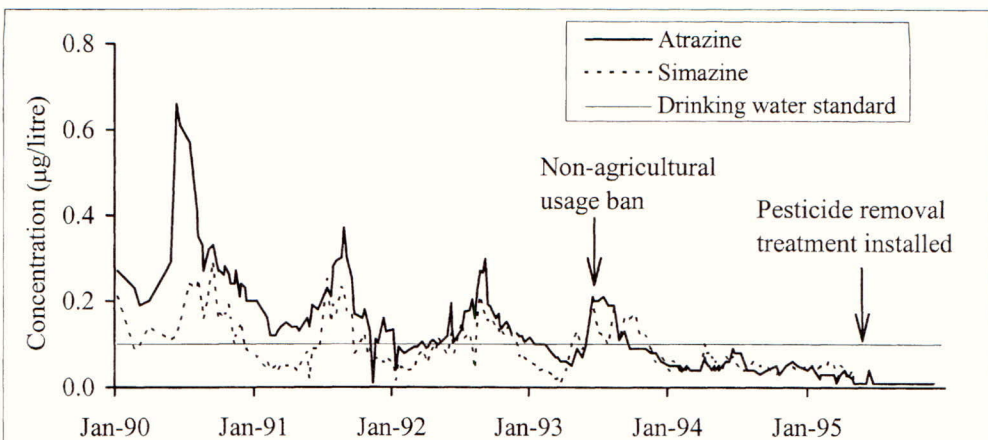


Figure 1. Atrazine and simazine in river Thames derived drinking water

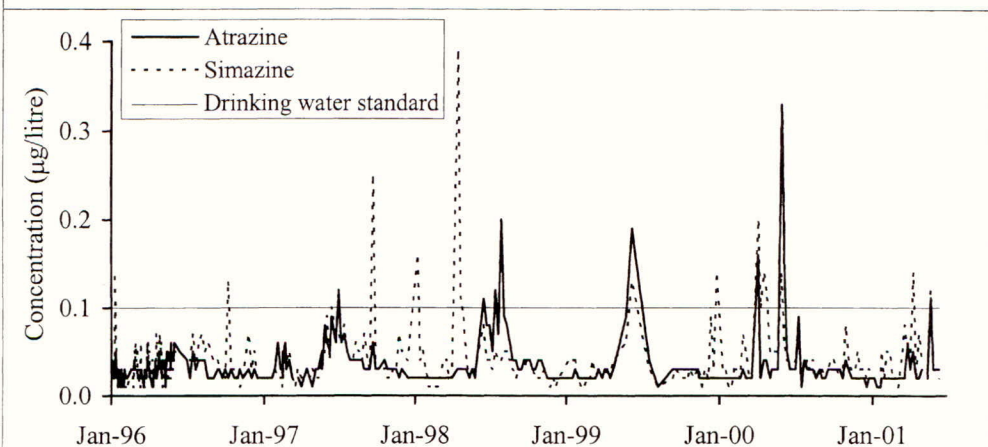


Figure 2. Atrazine and simazine in the river Thames at Walton

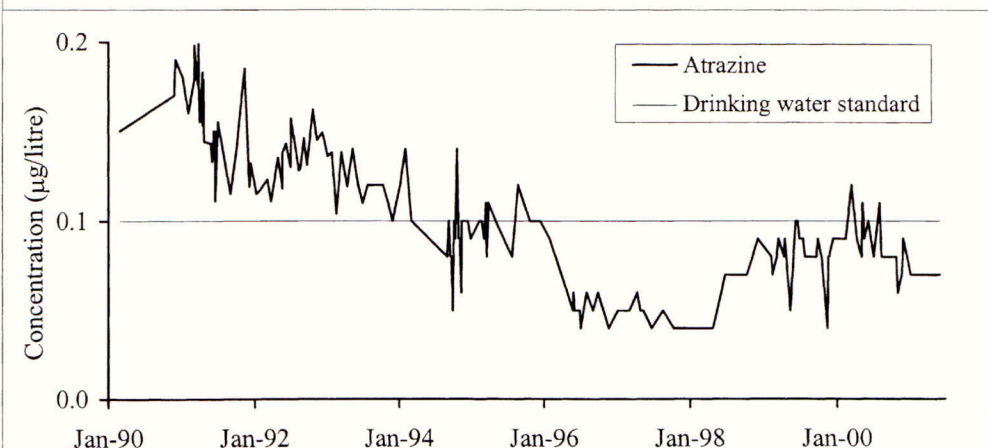


Figure 3. Atrazine in a rural groundwater source

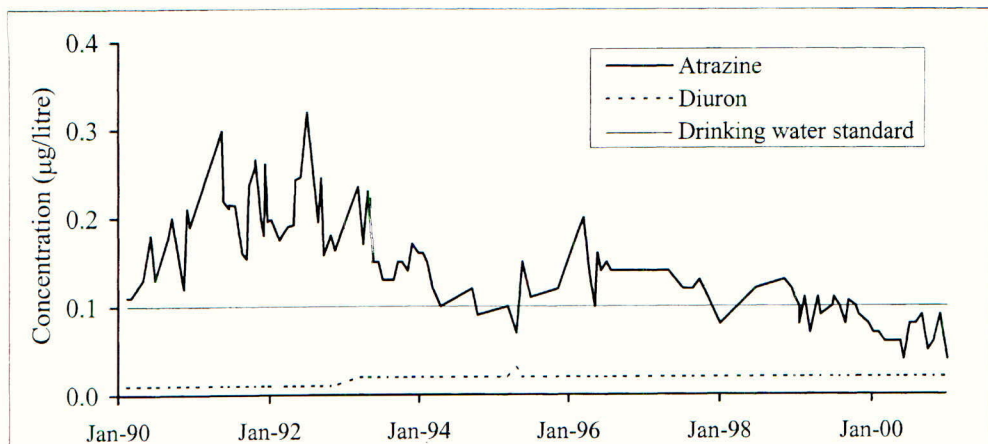


Figure 4. Atrazine and diuron in a groundwater close to a railway line

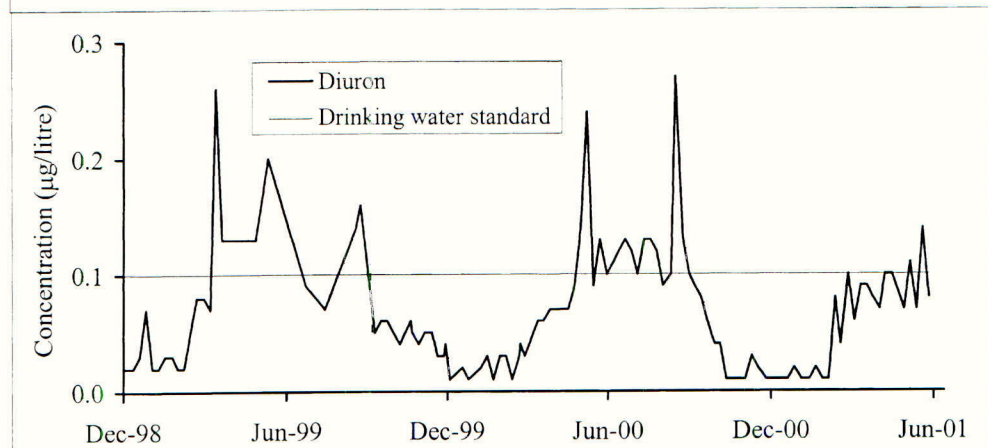


Figure 5. Diuron in the river Thames at Walton

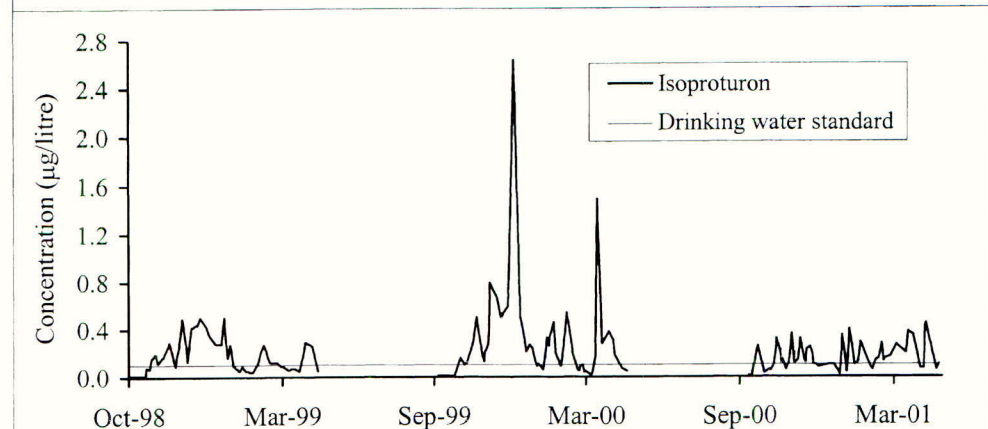


Figure 6. Isoproturon in the river Thames at Walton