

Chapter 4

Discriminating between Point and Non-Point Sources of Atrazine Contamination of a Sandy Aquifer

4.1 Outline

This study analyses the sources of atrazine contamination in the Brusselian sandy aquifer of central Belgium. Atrazine has in the past been used for both agricultural and non-agricultural applications, but it is difficult to distinguish the contamination originating from these two sources. The spatial and temporal covariance of atrazine concentrations was studied by fitting semivariogram models to monitoring data. Correlation ranges were found to be 600 metres and 600-700 days respectively. The results were used to apply a declustering algorithm before examining the distribution of atrazine concentrations measured in groundwater. Monitoring data appeared to follow a pseudo-lognormal distribution, as a lognormality test was negative. An inflexion point on the cumulative density function was thought to indicate the two different pollution processes, i.e. agricultural and non-agricultural contamination sources. A non-parametric one-way analysis of variance suggested that the vast majority of atrazine in groundwater was from non-agricultural, point sources. This was supported by the strong relationship between mean concentrations and land use, whilst other environmental variables, such as soil organic matter or groundwater depth, produced less meaningful results¹.

¹This chapter is based on an article by Leterme B., Vanclooster M., Rounsevell M.D.A. and Bogaert P. (2006); published in *The Science of the Total Environment* 362, 124-142.

4.2 Introduction

Contamination by pesticides has become a widespread problem for many groundwater bodies used for drinking water extraction. In accordance with the 91/414 European Directive (European Commission, 1991), pesticide concentrations may not exceed $0.1 \mu\text{g/L}$ for a single product and $0.5 \mu\text{g/L}$ for all compounds. Amongst the range of pesticides found within aquifers, atrazine (2-Chloro-4-ethylamino-6-isopropylamine-s-triazine) is one of the most problematic. Atrazine concentrations above $0.1 \mu\text{g/L}$ have been reported in many European and American regions (e.g. Rupert, 1998; Burkart et al., 1999a; Worrall and Besien, 2005). A particular feature of atrazine is that it can be used as a herbicide for both agricultural and non-agricultural purposes. Agricultural use is mainly devoted to maize and soybean cropping whilst non-agricultural applications include railway track treatment, urban weed control programmes or individual use in gardens. Point source pollution also includes spills from agricultural sources. In this study, the use of atrazine on agricultural crops is referred to as non-point pollution because in comparison, other uses are restricted to small areas (point sources). It is important to discriminate between point and non-point pollution sources for pesticides to design appropriate pollution risk mitigation strategies.

The environmental concentrations of many diffuse pollution source compounds are often found to have lognormal distributions. There are numerous examples of this for different environmental measurements, including ambient air quality data, pollutants in groundwater and radionuclides in soils (Ott, 1990). Groundwater bodies have often been characterised by relating hydrogeological processes to the distributions of different compounds. Edmunds et al. (2003) plotted cumulative probability diagrams to define baseline characteristics of groundwater. They argued that geochemical distributions might be polymodal and need to be interpreted in terms of the hydrogeology and/or hydrogeological processes. Examination of the spatial and temporal distributions of measured concentrations can help in discriminating between point and non-point pollution sources, e.g. a bimodal distribution would suggest either two different processes or different subsets of monitoring stations. Kunkel et al. (2004) presented a methodology in which geochemical distributions were systematically decomposed into two parts: a lognormal, background component; and a normal, anthropogenic contri-

bution. Whilst this method could be appropriate if two peaks were clearly distinguishable, considerable uncertainty would be expected if the distribution did not display a bimodal distribution. Runnells et al. (1998), cited by Edmunds et al. (2003), used probability plots to identify background and anthropogenic populations of elements in surface and groundwater samples. In the case of pesticides, the issue is different as there is virtually no background pollution, but questions may still arise as to the origin of contamination, as discussed in the present study.

A common approach to determine the origin of contamination is to identify significant relationships between groundwater pollution and environmental variables. Different studies have tested the influence of a number of environmental factors on the detection of a range of compounds (e.g. Teso et al., 1996; Worrall and Kolpin, 2004), but few studies have investigated the link between atrazine contamination alone and agricultural land use. Maas et al. (1995) found negative results when correlating atrazine levels within wells with a range of explanatory variables, although they worked with a relatively small data set that could mask such relationships. The variables considered were the distance to the nearest pesticide mixing, storage, and loading area; the distance to the nearest crop; the percentage of row crop in the nearest acre; and the well depth. Kolpin (1997) found significant correlations between atrazine-residue concentrations in shallow aquifers and several factors compiled from buffering zones around the sampling wells. The most important correlations were observed with the amounts of irrigated crop production, soybean production, rowcrop production and agricultural crop production. Indirectly, the relationship between atrazine concentrations and agricultural land use could be tested through the use of other variables, such as soil organic matter content. The significant negative correlation found between atrazine concentrations in the aquifer and organic matter in the upper soil layer (e.g. as in Burkart et al., 1999b), suggested that atrazine leaching was probably from agricultural, non-point sources rather than from point sources.

The aim of this chapter is to determine, for a specific case study, the respective contributions of point and non-point sources of atrazine to the contamination of a sandy aquifer. The methodology is based on the use of semivariograms, the examination of cumulative density functions and histograms and an analysis of variance.

4.3 Data and methods

4.3.1 Atrazine monitoring data

The Brusselian sandy aquifer is situated in central Belgium (see Figure 4.1(a)). A short description of this aquifer and land use in the study area was given in chapter 3.

Maize is the main crop that has received atrazine applications (Fytoweb, 2004), although atrazine is also used to protect asparagus and some orchards (Anonym, 1996). The asparagus and orchard areas are, however, negligible (INS, 2002). Non-agricultural use of atrazine was forbidden in the Walloon Region from 1992, but in practice it is difficult to control if (or when) applications completely ceased. National statistics indicate that atrazine sales for non-agricultural purposes represented about 25% of total sales over the last 20 years (CERVA, 2004). It is possible that individual users have bought stocks of atrazine from farmers to bypass the law on non-agricultural applications. In September 2004, all herbicides containing atrazine as an active substance were removed from sale, but their application for agricultural use is still authorised until September 2005 (Fytoweb, 2004).

In this study, the data set of atrazine concentrations was compiled from 97 monitoring stations (Figure 4.1(b)), including wells, galleries and sources. Most of the stations (i.e. wells and galleries) were operated to provide drinking water. Regional authorisation for drinking water exploitation is subject to the analysis of the presence of pesticides at least once a year. However, some monitoring points were more frequently sampled after pollution problems were detected. In total, 983 data points with atrazine concentrations were available for a period from 1989 until 2004.

4.3.2 Data censoring

Pre-processing of the groundwater monitoring data was necessary because of values ‘below the detection limit’. These types of data are subsequently referred to as ‘censored data’. Detection limits (DL) vary between atrazine monitoring data because groundwater samples were analysed by seven different laboratories and laboratory techniques have evolved over time. Data

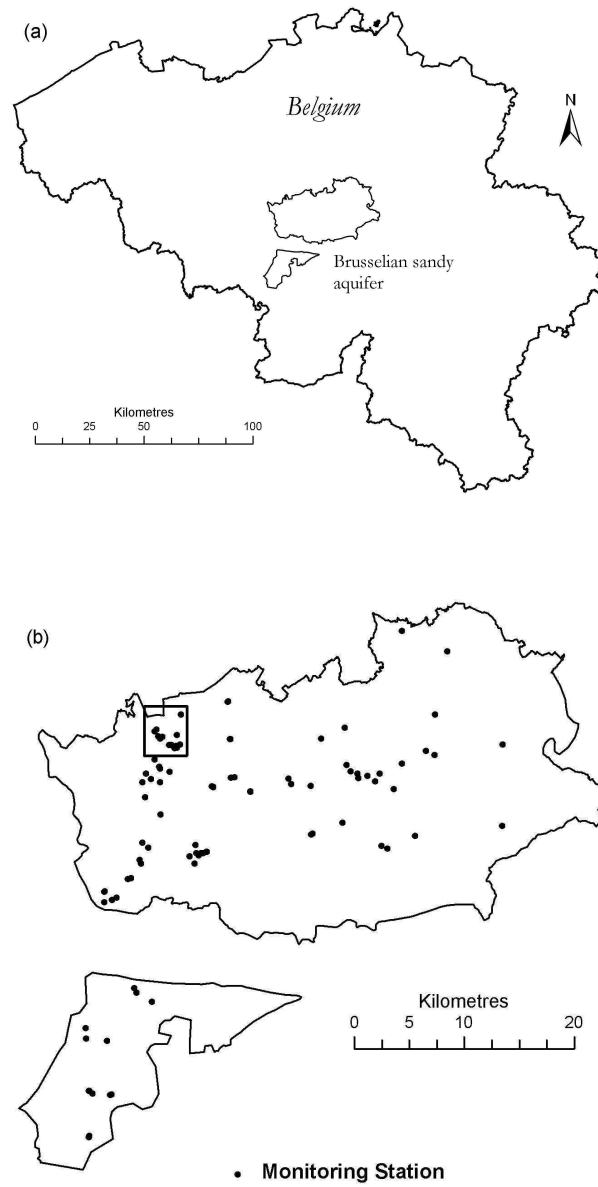


Figure 4.1: (a) Location of the Brusselian unconfined sandy aquifer in Belgium. (b) Location of the 97 monitoring stations supplying measurements of atrazine concentration in the Brusselian aquifer. The rectangle delineates the location of Figure 4.2.

quality was investigated by interviewing the people involved in sample analysis from the different laboratories. It was concluded that the three main laboratories that are officially recognized by regional authorities (and who provide more than 90% of the monitoring data set), have delivered high quality monitoring data.

Several methods exist to deal with censored values in a given data set. These include substitution with a constant, distributional methods, and robust methods (Helsel, 1990). Simple substitution methods substitute a single value such as one-half of the reporting limit for each value below the detection limit (the value is denoted as ' $<DL$ '). These methods are widely used, but have no theoretical basis. They are, however, preferred when the assumption of normality or lognormality of monitoring data is not met, or for very small data sets ($n < 10$; Farnham et al., 2002). Distributional methods use the characteristics of an assumed distribution (generally normal or log-normal) to estimate summary statistics. An important assumption is that the inferred distribution remains valid in the ' $<DL$ ' region. Robust methods combine observed data above the DL with ' $<DL$ ' extrapolated values, assuming a distributional shape, in order to estimate summary statistics. The most appropriate technique depends mostly on the application requirements. The best method for a given situation generally depends on the amount of data below the detection limit, the size of the data set and the probability distribution of the measurements (Farnham et al., 2002).

In this study, the procedure applied by local management authorities was followed. The method is based on simple substitution with different constants. A general DL of 25 ng/L was fixed as a broad 'common detection limit'. Then, individual censored data were replaced by $DL/2$ or $DL/4$ (i.e. by 12.5 or 6.25 ng/L), depending on their level of censoring. Null measurements were substituted by $DL/4$, while censored data with a detection limit smaller than 25 ng/L were replaced by $DL/2$. Other censored data were filtered out. The use of this substitution method can be justified in the case of atrazine, as two thirds of the monitoring stations have less than 10 data points, thereby preventing the application of alternative methods. Moreover, optimal methods, such as distributional methods, are intended to process the data for statistical hypothesis testing (e.g. detection of a significant temporal trend or the comparison of mean concentrations between two stations) or for the derivation of summary statistics. In the present

study, the computation of semivariograms also made use of the substitution method because data from different monitoring stations were used on an individual basis.

4.3.3 Spatio-temporal semivariograms

Semivariogram analyses were used to study the spatial and temporal dynamics of atrazine groundwater concentrations. As the case study deals with a sandy, porous aquifer, it was expected that atrazine concentrations would exhibit a spatial and temporal correlation structure. This information was needed to assess the spatial and temporal dependency of atrazine concentrations in groundwater. Atrazine concentrations in groundwater were defined as the variable of a random field. Under intrinsic second order stationarity, which assumes a constant mean across the random field, the semivariogram function γ allows an evaluation of the variance of the difference between values at different distance lags:

$$\gamma(h) = \frac{1}{2} \text{var}[Z(x_i + h) - Z(x_i)] \quad (4.1)$$

where h is the distance lag between two points and $Z(x_i)$ is the random field in location x_i .

For the calculation of a spatial semivariogram, it is necessary to assume that data measurements were made simultaneously. Thus, the time interval for measurements was kept as short as possible, but still large enough to allow for a sufficient number of ‘simultaneous’ pairs of points. Semivariograms were calculated at each time interval and then averaged.

For the temporal analysis, semivariograms were calculated for every monitoring station and then averaged (weighted by the number of data points per station).

Information on the groundwater depth of sampling points was not available. Therefore, it was not possible to look for a possible influence of groundwater depth on atrazine concentrations dynamics. Besides, the analysis was repeated without the infiltration galleries to verify if they could have an influence on the results.

All calculations were made in MatlabTM, using the geostatistical BMElib package (Christakos et al., 2002).

4.3.4 Influence of censored data on the semivariogram range

The substitution of censored data by constant values could influence the derivation of spatial and temporal semivariograms. To investigate this, synthetic random field realisations of atrazine concentrations were simulated on a 3000×2500 m surface (50×50 m square grid cells). This area was considered to be large enough to simulate correlation ranges not greater than 1000 metres. Gaussian data were transformed into pseudo-lognormal distributions using a monotonic transformation based on the cumulative density function of the real data set. These random fields had a spatial correlation structure represented by several types of models (spherical, exponential, nugget + exponential). Sixteen monitoring stations were randomly located within this area (thereby giving approximately the same monitoring density as in the study area), with the condition that a sufficient number of pairs of points were present at each distance class. Several (e.g. 20, 100 or 250) realisations of this random field were then generated to replicate the situation where spatial semivariograms were calculated at different time intervals (cf. the above assumption of simultaneity). Pseudo-monitoring data were collected at the 16 monitoring points and an arbitrary detection limit was established to produce a data set having a certain percentage of ‘below detection limit’ data. The censored data thus obtained were replaced by a substitution value (zero, $DL/2$ and DL were tested). The semivariogram analysis was then performed on this synthetic data set in order to determine how well the fitted parameters (sill and range) related to the model used for generating the data. This exercise was repeated for different configurations of the following parameters: the number of simulated random fields (analogous to the number of time intervals in the ‘real’ data set), the semivariogram model, the substitution constant and the detection limit (i.e. amount of censoring).

The same analysis was performed for the temporal semivariogram, except that the number of simulated random fields corresponded to different monitoring stations for which the semivariograms were calculated.

The main results are presented in section 4.4.1, including both the fit-

ting of spatial and temporal semivariograms to experimental data and the analysis of censoring effect on a synthetic data set.

4.3.5 Cumulative density function and histogram analysis

The spatio-temporal distribution of atrazine concentrations was examined using cumulative density functions and histograms. However, the data set of atrazine concentrations presented above could not be assumed to contain independent samples. Monitoring data that are collected at small distances of separation in both space and/or time do not respect the condition of independence. Thus, two samples collected at an interval of one day should be considered as replicates rather than distinct samples because atrazine concentrations in groundwater are not expected to change significantly over a very short period of time. The spatial and temporal semivariogram analyses described above allowed the derivation of models and parameters that reflect the correlation structure of atrazine concentrations in the aquifer. These models were used to apply a declustering algorithm to the monitoring data and hence to ensure the independence of the data.

The basic principle of a declustering algorithm is to affect different weights to the data, which are directly related to the variogram models. For the spatial part of the analysis, monitoring stations that are located close to each other were given a smaller weight because their monitoring data were expected to have similar values and hence to introduce repetitions into the data set. For the temporal analysis, successive data within a monitoring time series were given a lower weight, whilst data outside of the correlation range of another sample were given the maximal weight. For each monitoring station, the cumulative sum of ('temporal') weights was fixed at 1, thereby giving all monitoring station the same weight in a first time, whatever their number of samples. These 'temporal' weights were then multiplied for every data by the 'spatial' weight of its corresponding monitoring station. An example of 'spatial' weights for a cluster of monitoring stations is shown in Figure 4.2. Thus, for a given monitoring station, the sum of weights of the monitoring data is equal to the 'spatial' weight of this monitoring station:

$$\sum_{i=1}^n w_{i,j} = S_j \quad (4.2)$$

where $w_{i,j}$ is the weight of the i^{th} sample data of the monitoring station j ; and S_j is the ‘spatial’ weight of monitoring station j . The total sum of declustering weights for all the data in the study area is equal to one, i.e.

$$\sum_{j=1}^N S_j = 1 \quad (4.3)$$

where N is the number of monitoring stations.

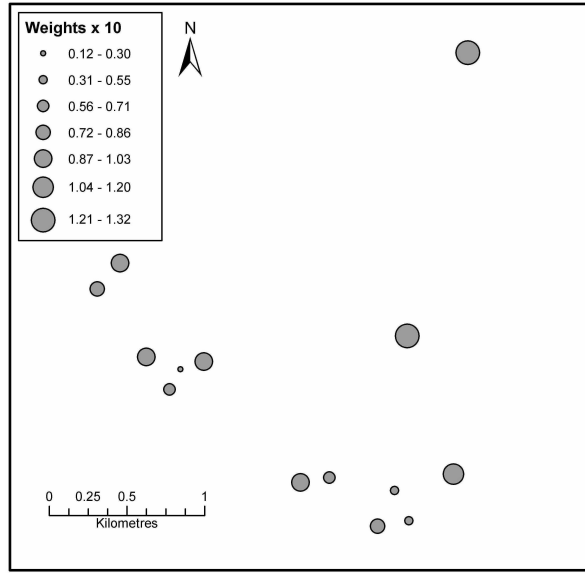


Figure 4.2: Example of spatial declustering weights (the rectangle in Figure 4.1(b) shows its location within the study area).

Using these declustering weights, the cumulative density function (CDF) of atrazine concentrations was plotted to assess the fit of monitoring data against a lognormal distribution. It was hypothesised that any significant deviation from this theoretical distribution would be due to point source within the general trend of diffuse leaching.

4.3.6 Analysis of variance

A one-way analysis of variance (ANOVA) was performed on the data set to test the ability of different variables to explain the spatial variability of

atrazine concentrations in the aquifer. The time mean concentration of each monitoring station data was taken as the dependent variable. In a one-way ANOVA, different populations were compared through a statistical procedure in which the total variation in a measured response was partitioned into components that can be attributed to the treatment effect or to an error term (Milton and Arnold, 2003). The independent variables, described hereafter, were classified to form the different treatments against which the measured response (mean atrazine concentration) was tested.

Nonparametric one-way analysis of variance (Kruskal-Wallis test) was performed because of the non-homogeneity of the variance between treatments when monitoring stations were grouped. Assume that k independent random samples of sizes $n_1, n_2, \dots, n_k$ are drawn from a continuously distributed population. The Kruskal-Wallis procedure tests the null hypothesis that each of the k samples was drawn from identical populations (Milton and Arnold, 2003). In this study, the test was used to check whether a certain variable could explain the variability in atrazine groundwater concentrations. To test the null hypothesis, the monitoring stations were classified into k samples according to the variable that was considered. If the null hypothesis of identical populations is rejected, then the variable in question certainly has an influence on the differences in atrazine concentrations. The Kruskal-Wallis (KW) test was modified to take the declustering weights into account. As the modifications concerned mean calculations (mean total rank and mean rank of each treatment), these did not introduce any bias into the calculation of the chi-square statistic.

In addition, Dunn's method (Hollander and Wolfe, 1973) was chosen to perform multiple comparison tests when the null hypothesis of the Kruskal-Wallis procedure was rejected. This allowed identification of the treatment that was significantly different from the other treatments.

The variables used in the analysis were: soil organic matter content in the plough layer, sand and clay contents in the plough layer, depth to groundwater, distance to the nearest road, distance to the nearest railway track, density of arable land use, density of urban land use. The soil variables were selected because they were shown previously to have had an important role in the observation and simulation of atrazine leaching from non-point sources (Flury et al., 1995; Persicani, 1996). Depth to groundwater was included in the analysis because this variable has frequently been used in

groundwater vulnerability assessments (Fogg et al., 1999). The land use variables were chosen to determine whether the different atrazine sources (agricultural and non-agricultural) could be directly linked to groundwater contamination.

Data on soil properties were derived from the Aardewerk soil profile database (Van Orshoven and Vandenbroucke, 1993). This database consists of more than 10,000 detailed soil profile descriptions (i.e. texture, organic matter, pH, etc. for the different soil horizons) in Belgium. The Aardewerk points are not evenly distributed, but 650 profiles were available within the arable part of the study area. Only soil profiles with arable land use were considered because the soil variables were taken as indicators for testing groundwater contamination from agricultural sources. For example, since atrazine leaching is known to be highly dependent on soil organic matter (SOM) content (Wauchope et al., 2002), this variable was used to test if it explained the variability in measured concentrations. As Aardewerk profiles were not available at the exact location of monitoring stations, a nearest neighbour method was used to allocate soil properties (SOM, sand and clay content in the plough layer) to each monitoring station. The mean distance between a monitoring station and the nearest Aardewerk arable profile was 1179 metres. For SOM contents, it was possible to use ordinary kriging as an alternative method for allocating values to the monitoring stations because spatial autocorrelation occurred and a semivariogram model was found to be a good fit to the data (nugget + exponential model, correlation range around 3000 metres). A consistent semivariogram could not be fitted to the soil texture data, thereby limiting the allocation method to a simple nearest neighbour approach.

A spatial layer of depth to groundwater (not taking into account pumping conditions) was obtained by using a digital elevation model (DEM), Brusselian isopach data (Monteyne, 1986) and piezometer data (maximum water level in time series, to obtain the superior limit of water table; DGRNE, unpublished data). The highest value in the time-series of piezometer data was taken as a 'hard' data point. Interpolation of these data points, using the Bayesian Maximal Entropy interval mode in BMELib (Christakos et al., 2002), was conditioned by an interval defined by the difference between the DEM and the lower boundary of the Brusselian sands. The resulting grid layer of groundwater level was subtracted from the DEM (rescaled to 500 m

resolution) to obtain the variable groundwater depth. Piezometer and thus groundwater depth data were not available for the whole study area, but were obtained for 74 monitoring stations corresponding approximately to the major northern part of the aquifer (see Figure 4.1(b)). This methodology was developed elsewhere (Pinte et al., 2005) and adopted in the present study as the best available approach to estimate groundwater depth.

Distances to the nearest road and to the nearest railway track were calculated from a regional database of the transport network. Land use data were obtained by merging detailed parcel pattern data (resolution 100 m; source: Système Intégré de Gestion Et de Contrôle (SIGEC), 1999) from the 1999 agricultural census with a classified Landsat TM image of 1999. Since the SIGEC map (SIGEC, 1999) overlaps only half of the monitoring stations, it was not possible to use detailed agricultural land use classes (i.e. individual crops) as independent variables in the ANOVA. Land use classes were aggregated therefore to produce, amongst others land uses, arable and urban land use maps (resolution 100 m). Land use densities were then calculated with circular neighbourhoods of different radii. Again, land use data were only available for 81 monitoring stations.

4.4 Results and discussion

4.4.1 Spatial and temporal semivariograms

Some stations have atrazine concentrations that are very much higher than the rest of the data set and this causes problems for the semivariogram computation. In some instances, atrazine concentrations were 20 times more than the authorised limit ($0.1 \mu\text{g/L}$). The data for these stations (164 measurements from four stations, corresponding to 17% of all the measurements and 4% of the monitoring stations), were removed from the analysis because it was thought that they reflect localised hot spots of non-agricultural contamination that are not consistent with the study aims of finding the general spatial and temporal dynamics of contamination. This assumption was later confirmed. The spatial semivariogram of atrazine concentrations is presented in Figure 4.3(a). The spherical model fitted to the data has a correlation range of about 600 metres. A detailed analysis of the semi-variance in the first distance class (0-200 m) was made to evaluate confidence in the

results because fitting a model depends heavily on this first distance class. It was found that seven distinct sites provided data for the first distance class. Thus, the number of data points and the similarity of the simultaneous measurements were sufficient to be confident about the shape of the experimental semivariogram. The lower semi-variance of distance class 800-1000 m (see Figure 4.3(a)) was probably due to the lower number of monitoring stations within this class.

The temporal semivariogram shown in Figure 4.3(b) was calculated from detrended data (by polynomial fitting) and without the monitoring stations with obvious outliers. The temporal correlation range was found to be from about 600 to 700 days, although this value must be taken merely as an indication of its order of magnitude. The lower semi-variance observed at time lags of between 900 and 1400 days seemed to be due to limitations in the sampling regime. A group of monitoring stations had a period of 900 days without any sampling. Therefore, for each of these monitoring stations, pairs of points separated by more than 900 days were over-represented and produced lower semi-variance values. When this group of stations was removed from the analysis, the lower semi-variance values did not occur, but the temporal correlation range fitted to the data was still found to be around 700 days.

Comparing the values at the plateau in the spatial and temporal semivariograms (circa 750 and 1.2, respectively; Figure 4.3) is not relevant, because a weighting of the monitoring stations had to be included in the temporal analysis. Therefore, the values at the plateau cannot be compared and this difference is underlined by the γ^* symbol on Figure 4.3(b).

4.4.2 Influence of censored data on the semivariogram range

An important issue before using these results was to verify the influence of data censoring on the derivation of semivariograms. Figures 4.4(a) and (b) display some results of the sensitivity analysis performed on the synthetic data set. In Figure 4.4(a), 250 random fields were simulated using a spherical semivariogram model and spatial semivariograms were fitted at each monitoring set (16 stations) before averaging, as for the methodology with the real data set at different time intervals. This was done with an increasing arbitrary detection limit to observe the effect of censoring. Figure 4.4(a)

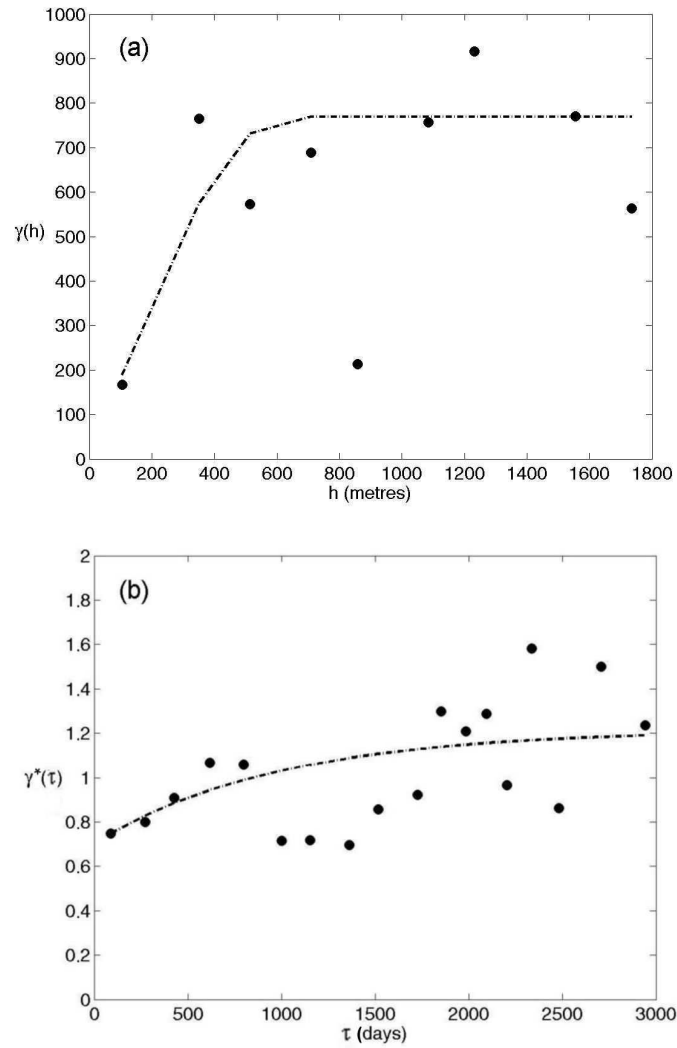


Figure 4.3: (a) Spatial and (b) temporal semivariograms of atrazine concentrations in groundwater. Dashed lines show the spherical and exponential (with a nugget effect) models that were fitted to the calculated semi-variances (points).

shows that below 20% censoring, the effect on the fitted correlation range is negligible. Since the real data set for the Brusselian aquifer contained only 9% censored monitoring data, these results (and others not shown here) exclude the influence of censoring on the derivation of the spatial semivariograms. Moreover, the substitution with different constants indicated that $DL/2$ is the most robust value with increasing amounts of censoring. The results were found to be similar for the temporal part of the simulation exercise. Figure 4.4(b) displays the results of the simulation exercise performed on 60 time series (corresponding to different monitoring stations), which were generated using a combination of nugget and exponential semivariograms. Again, the influence of censoring was not significant below 20% of censored data, and $DL/2$ was a good substitution method. These results are consistent with the evaluation of the efficiency of substitution methods in principal components analysis (Farnham et al., 2002).

The results of the semivariogram analysis (spatial and temporal correlation ranges of 600 m and 600-700 days) should not be regarded as exact values since the data were not based on a carefully designed experiment, but rather as indications of the correlation structure. These values are believed to be representative of atrazine concentrations in the Brusselian aquifer. Different sources of uncertainty were considered before using these values for the declustering algorithm. The uncertainty deriving from monitoring data quality was assumed to be negligible as it was observed that the vast majority of data were analysed by high quality laboratories. As no information was available on sampling quality, it could only be assumed that sampling protocols were correctly applied. The presence of infiltration galleries in the set of monitoring stations had no influence on the results. Uncertainty from data censoring was also shown to be of no consequence. The semivariogram fit was believed, therefore, to be the main source of uncertainty. A further source of uncertainty derives from the data being collected at different depths in the aquifer. It was not possible to know the depths at which water was pumped for all monitoring wells. Data on the stratification of herbicide concentrations in the aquifer are rare and results for the experimental sites where this issue has been investigated suggest that incorporating such complexity would be difficult at the scale of the study presented here (Hallaux, 1995). However, detailed analysis of the semi-variance for the first few distance classes suggested a significant correlation structure, which was

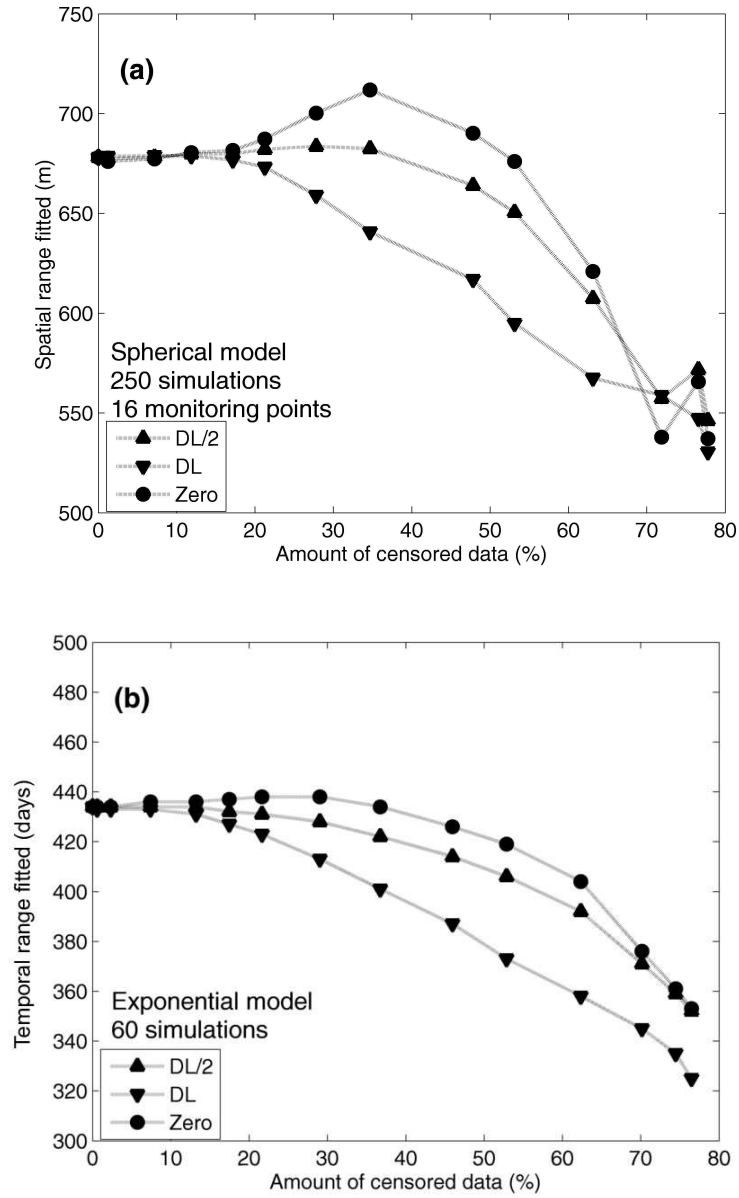


Figure 4.4: Influence of the amount of censored data and three different substitution constants (DL/2, DL and zero) on the fit of (a) spatial and (b) temporal correlation ranges using semivariograms models on a simulated data set. Note that the vertical axes do not start at zero.

an indication that data quality was satisfactory for the goals of the present study.

4.4.3 Cumulative density function and histogram analysis

Figure 4.5(a) shows (on probability paper) a plot of the cumulative density function (CDF) of the whole data set without any modification. The gap around the 5th percentile is due to the substitution of censored data with $DL/4$ ($= 6.25$ ng/L; substitution method adopted by management authorities). A striking feature of the CDF and the corresponding histogram (Figure 4.5(b)) is the roughly bimodal form resulting from a horizontal shift in the curve around the 80th-90th percentiles. It is possible that this bimodal form is an indicator of two different contamination processes, e.g. agricultural and non-agricultural pollution sources.

However, these simple CDF plots and histograms contain significant bias for two reasons. The first is that all monitoring stations do not provide the same quantity of samples. Some monitoring stations have only one data point, whilst others have more than 40 samples. The stations with more data points are thereby much more important in determining the general shape of the CDF and histogram. A second factor is the correlation in both space and time between monitoring data, which was shown by the semivariogram analysis. It is likely that if two monitoring stations are located 30 metres from one another and were sampled simultaneously, they would probably have similar atrazine concentrations. Likewise if two samples were taken at very short time intervals they would also probably be similar. This clearly had an impact on the shape of the distribution.

After the declustering weights (section 4.3.5) were applied to the monitoring data, new unbiased CDFs and histograms were computed. Figure 4.6(a) shows this ‘declustered’ CDF plot with the theoretical CDF of a log-normal distribution (dashed line). The experimental CDF of Figure 4.6(a) and the corresponding histogram (Figure 4.6(b)) can be seen as optimal representations of the distribution of atrazine concentrations in groundwater, aggregated over the monitoring period. Clearly, the CDF can no longer be interpreted as a bimodal distribution. Yet, the effects of data censoring are still visible in the first 10-15 percentiles of the distribution, particularly at

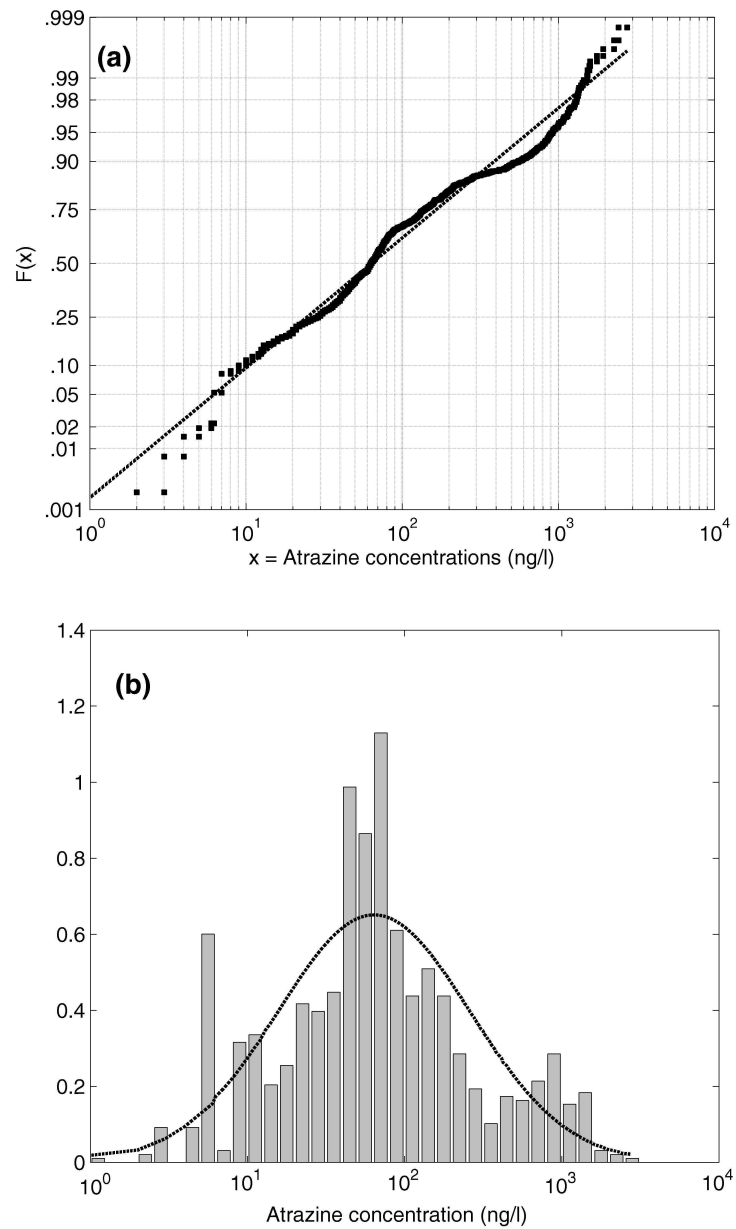


Figure 4.5: (a) Cumulative density function and (b) histogram of the complete set of atrazine concentration data. Dashed line is the null hypothesis of a lognormal distribution. Note the logarithmic scale of x-axes.

a value of 6.25 ng/L, which was used as the substitution constant for most of the censored data.

From this point, the CDF curves slightly upwards in a regular way, with a slow, but steady increasing gap to the theoretical CDF. The smooth curve is interrupted between the 90th and 95th percentiles, where concentrations show a sharp increase. The CDF then curves up again, but a similar sharp increase occurs for a second time at the end of the CDF. These two sharp upward deviations (the first of which cannot be detected in Figure 4.5(a)) mean that the CDF is almost parallel to the theoretical CDF of a lognormal distribution (dashed line). Yet, a Kolmogorov-Smirnov test rejected the null hypothesis of a lognormal distribution, due to the vertical gap between the two CDF curves. The vertical shift is due to the unique substitution constant used (6.25 ng/L). Some laboratories provided exact measurements below 6.25 ng/L thereby explaining the presence of data below this value.

However, the significant abundance of censored data in the declustered distribution and the resulting horizontal shift around the 15th percentile (Figure 4.6) can be explained. It is suggested that some monitoring stations provided <DL data not because atrazine applied at the surface was adsorbed or decayed before reaching the water table, but because atrazine was not applied at the surface above these monitoring stations, nor within their capture zones. In 1999, urban areas (16%) and maize cropping (between 3 and 4% of land use) combined covered less than 20% of the study area. Even though groundwater transport has to be taken into account (cf. spatial correlation range ~620 metres), large areas have not had atrazine applications and therefore a number of monitoring stations will inevitably measure null atrazine concentrations. If atrazine leaching was shown to be mainly from agricultural sources, crop rotations over the years might spread atrazine inputs in space. In the study area, maize is generally grown in 3-year rotations with wheat and barley, or sometimes as a monoculture (Ledent, 2003). Nevertheless, in such cases, crop rotations would only slightly affect surface applications, as the total arable area was about 45% of the study area in 1999, and not all arable areas include maize in rotation.

Whilst the application of a declustering algorithm enabled monitoring data to provide useful information about the distribution of atrazine concentrations in groundwater, a statistical analysis was needed to discriminate between agricultural and non-agricultural contamination sources.

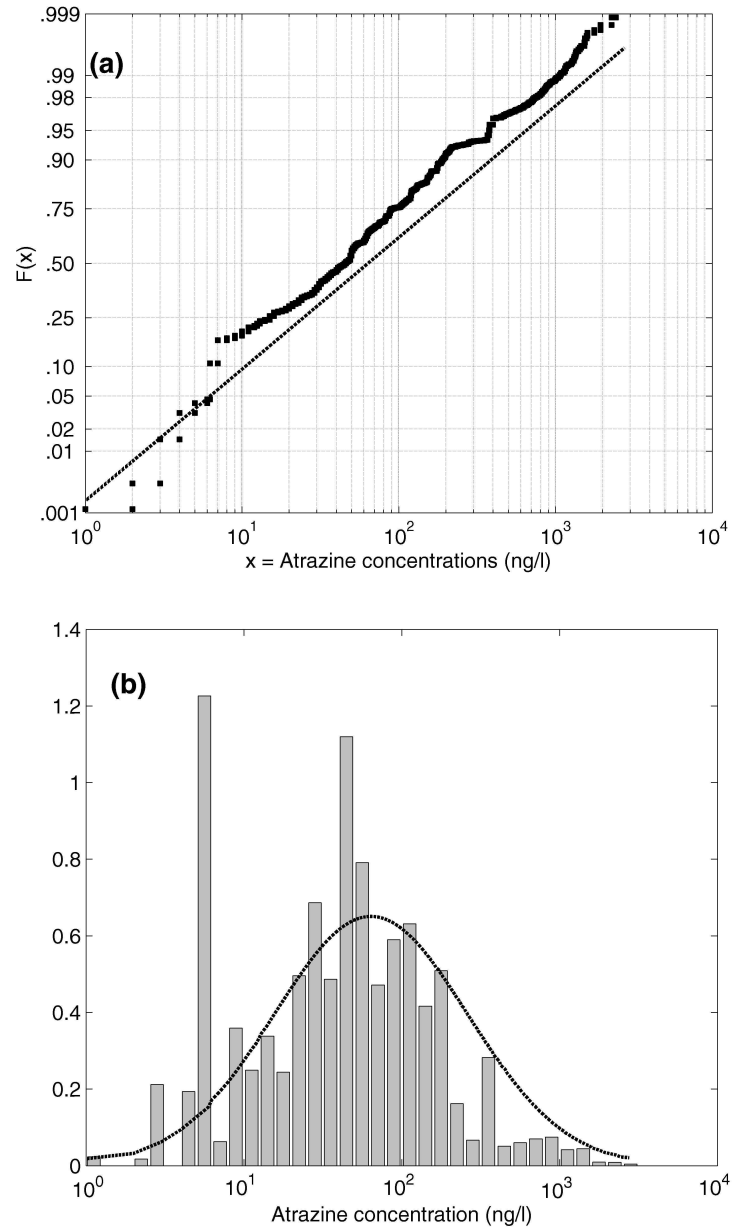


Figure 4.6: (a) Cumulative density function and (b) histogram of the complete set of atrazine concentration data after the application of the spatial and temporal declustering algorithms. Dashed line is the null hypothesis of a lognormal distribution. Note the logarithmic scale of x-axes.

4.4.4 Analysis of variance

The Kruskal-Wallis (KW) tests took the declustering algorithm into account and were performed on the complete (given data availability for some variables) set of monitoring stations. Further analyses used a subset of stations excluding those with one or more sample(s) above 220 ng/L. This was done to check if discontinuity in the CDF could be attributed to different leaching processes (i.e. non-agricultural vs. agricultural sources) or to a different population of atrazine concentrations. The cut-off value of 220 ng/L was chosen because it is the inflexion point of the CDF curve (Figure 4.6(a)), above which most of the monitoring data come from a specific area where the non-agricultural origin of contamination was clearly highlighted (Debondgnie et al., 1996). This selection removed 14 monitoring stations from the analysis. Moreover, that the significance of the KW test improved by removing these stations suggests that two different populations are being considered.

The results of the KW tests are presented in Table 4.1. The first factor used as an independent variable was the percentage of SOM in the plough layer of arable soil profiles. SOM change since the 1950s (when the data were collected) was not taken into account. Correction factors for each soil association and land use are given by van Wesemael et al. (2004), but this would have no incidence on the results because soil properties were examined for arable land use only and the correction factors would have been very similar across the study area. SOM contents were classified in five treatments, i.e. in classes 1 to 5 with increasing SOM content. The KW test was only significant ($p_v = 0.0276$) with the nearest neighbour method and the reduced set of stations (i.e. those having all samples below 220 ng/L), but only when detecting a higher mean rank (i.e. higher mean atrazine concentrations) for class 2 compared to classes 1 and 4. The relationship seemed logical between classes 2 and 4 (i.e. lower SOM content coupled with higher atrazine leaching), but was counter intuitive between classes 2 and 1. This result seemed relatively inconclusive because it contained contradictory indications and was only significant for one out of five classes compared to two other classes. Moreover, the different outcomes obtained with the kriging method raised doubts about the real significance of this result.

Two soil textural classes, sand and clay content in the plough layer, were

Table 4.1: Results of the Kruskal-Wallis tests for the mean concentration of atrazine (one-way Analysis of Variance). For each test, the number of treatment classes is equal to the number of degrees of freedom (df)+1.

Independent variable	Number of stations included (n)		df	p -value ($\text{Pr} > \chi^2$)
	All available	No data > 220 ng/L		
Soil organic matter	97		4	0.2674
(nearest neighbour)		83	4	0.0276
Soil organic matter	97		4	0.6836
(kriging)		83	4	0.1086
Sand	97		1	0.4808
(nearest neighbour)		83	1	0.0395
Clay	97		4	0.3860
(nearest neighbour)		83	4	0.3860
Depth to groundwater	74		3	0.0482
		65	3	0.0447
Distance to road	97		3	0.0354
		83	3	0.1552
Distance to railway	97		3	0.4155
track		83	3	0.8513
Density of arable LU	81		2	0.0096
($r = 300$ m)		72	2	0.0342
Density of urban LU	81		2	0.0010
($r = 300$ m)		72	2	0.0044
Density of urban LU	81		2	0.0372
($r = 200$ m)				
Density of urban LU	81		2	0.0181
($r = 500$ m)				
Density of urban LU	81		2	0.0107
($r = 1000$ m)				

tested to explain the variability in atrazine contamination. KW tests were not significant ($p_v = 0.4808$ and $p_v = 0.3860$ respectively for sand and clay contents) using the complete set of monitoring stations. However, when the analysis was restricted to the subset of '<220 ng/L' stations, the two sand classes (corresponding to silt and sandy or sandy loam soils) differed significantly ($p_v = 0.0395$), and this time in an intuitive way, suggesting that higher sand contents (i.e. increased drainage) in the upper soil horizon or soils with an eroded loess cover (i.e. unprotected aquifer) are associated with higher groundwater contamination by atrazine. Until this point, the study hypothesis remains plausible, i.e. that the subset of monitoring stations having samples below 220 ng/L are associated with diffuse atrazine leaching from agricultural sources, whilst the highly contaminated monitoring stations are related to non-agricultural atrazine applications.

Depth to groundwater was classified into 4 classes or treatments (increasing depths to groundwater from classes 1 to 4). When all available stations were considered, class 3 was found to have a significantly lower mean rank than class 4 ($p_v = 0.0482$), which is contrary to the common assumption that groundwater vulnerability decreases for deeper aquifers. Similarly, when only the subset of monitoring stations was considered, KW tests showed a significant difference between class 1 and both classes 2 and 4 ($p_v = 0.0447$). Again and surprisingly, lower groundwater depths were associated with less groundwater contamination.

Distance to roads (4 classes) was also analysed to test whether groundwater contamination was mostly caused by non-agricultural sources. The KW test was significant ($p_v = 0.0354$) when all the monitoring stations were included in the analysis, but only between treatments 3 and 4 (the two classes with the highest values of the distance between monitoring stations and the nearest road). Since these classes were defined respectively as the [300, 500 m] and >500 m intervals, it is unlikely that this significant test really indicates the influence of road-related atrazine applications in explaining groundwater contamination.

The distance to railway tracks was also tested using the KW test as it is known that railway tracks in the study area were treated with atrazine for weed control. However, the results were not significant ($p_v = 0.4155$ and $p_v = 0.8513$). This was not unexpected, as this type of atrazine application is limited in its spatial extent, independently of the application dose. Lo-

calised spots of atrazine leaching could possibly be linked to railway tracks in some cases, but at a regional scale this type of application cannot explain groundwater pollution to the extent observed here.

Although land use data were not available for the surroundings of all monitoring stations, KW tests performed with arable and urban land use densities had the most significant results. Arable land use density, calculated within a 300 m radius of monitoring stations, produced significant KW tests ($p_v = 0.0096$ and $p_v = 0.0342$), and the most significant result was obtained when all monitoring stations were included ($p_v = 0.0096$). Figure 4.7(a) compares the treatment mean ranks obtained in the KW test with different arable land use densities. It can be observed that most arable areas (>33% arable land use in the neighbourhood) were associated with lower mean ranks and hence, lower mean atrazine concentrations. Thus, arable areas, which are the most likely sources of atrazine leaching from agriculture, are in practice the least important in terms of groundwater contamination. This is an important result, as it clearly discounts agricultural applications as the major source of atrazine leaching to groundwater.

Density of urban land use, also calculated within a 300 m radius of monitoring stations, is not the inverse of arable land use because of other important land uses such as grassland and forests. However, urban land use density had highly significant results, both with and without the monitoring stations with sample(s) >220 ng/L ($p_v = 0.0010$ and $p_v = 0.0044$). Figure 4.7(b) compares the treatment mean ranks obtained in the KW test with different urban land use densities. A clear relationship appeared between urban land use density and the mean rank of the corresponding treatment, i.e. higher urban density was associated with higher mean ranks and hence, higher mean atrazine concentrations.

The sensitivity of the KW tests to the delineation of the land use density within the neighbourhood was tested both for arable and urban classes. Table 4.1 gives the KW results with varying radii for urban land use density. It can be seen that the KW tests remained significant for all values tested (200, 500 and 1000 m; $p_v = 0.0372$, $p_v = 0.0181$ and $p_v = 0.0107$ respectively).

The results of the Kruskal-Wallis tests on arable and urban land use densities strongly suggested that the atrazine contamination monitored in the Brusselian aquifer derives from non-agricultural sources for most of the

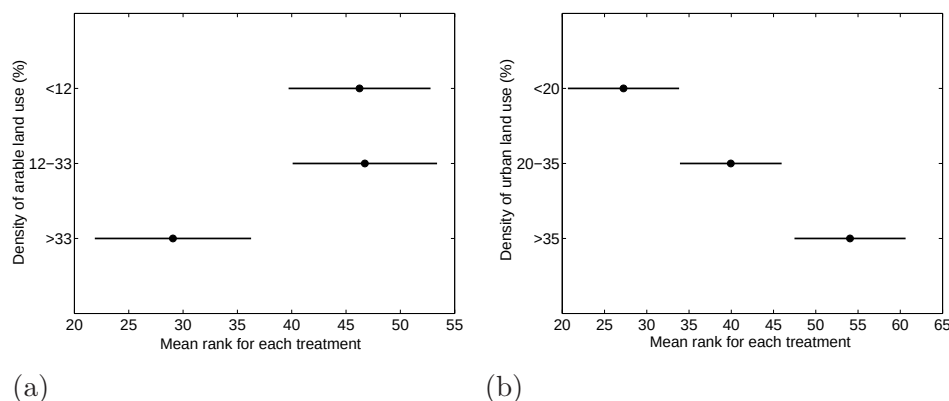


Figure 4.7: Multiple comparison of mean ranks for (a) arable and (b) urban land use. The horizontal bar gives the confidence interval of the treatment mean rank.

monitoring stations. These two variables had the most significant p -values and the clearest relationships with mean concentrations using Dunn's test. Moreover, several additional arguments support these findings.

First, the significant result of the variable distance to road can be seen as a confirmation of the main results, since the distance to the nearest road can be seen as a proxy for the variable urban land use density.

Secondly, the unexpected relationships found between depth to groundwater and atrazine mean concentrations suggested that the processes explaining groundwater contamination in this case did not comply with the conventional assumptions made for diffuse leaching processes from agricultural sources. However, despite the lack of quantitative data about the non-agricultural uses of atrazine, it is a quite plausible picture of the situation to imagine that for non-agricultural uses of atrazine, the quantities and timing of applications are much more variable, as are the types of application (treatment of railway tracks, municipal weed control programmes, application by individuals, etc.). CERVA (2004) indicated that non-agricultural doses of applications had been made up to 10 times higher than those of agricultural applications. The final groundwater contamination would therefore be more dependent on the application characteristics (dosage and timing) than on environmental variables such as depth to groundwater, or organic matter content. Localised hot spots of groundwater pollution could instead

be simply related to specific and heavy, point atrazine inputs.

Similarly, the significance of KW with SOM (allocation by nearest neighbour) involved only the relationships between one class and two others, with one relationship being contrary to what would be expected for homogeneous non-point pollution processes. The KW test of sand content, which was becoming significant when the stations with sample(s) >220 ng/L were removed, is the only result that might support the hypothesis of a few high contamination events from non-agricultural applications in parallel with agricultural sources providing the rest of the leached atrazine. However, sand contents were classified into only two classes, corresponding to the sandy and loamy soils. As sandy soils are generally located in the valleys of the study area, they are related to the presence of urban settings, which were shown to have a strong influence on groundwater contamination by atrazine.

Considering the subset of monitoring stations that are classified in the class >33% of arable land use density (class 3), their number were not sufficient to perform additional KW analyses in order to test the relationships with depth to groundwater, sand and organic matter contents.

A statistical analysis of the Walloon Region monitoring database was made by CERVA (2004). It was found that at the regional scale, the first four pesticides, in terms of the number of monitoring stations having samples above 20 ng/L, were compounds used for non-agricultural applications: atrazine, simazine (6-chloro-N,N-diethyl-1,3,5-triazine-2,4-diamine), diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) and bromacil (5-bromo-3-sec-butyl-6-methyluracil). This list reinforces the hypothesis that groundwater contamination by atrazine in the study area is predominantly from point sources.

The allocation of independent variables to monitoring stations did not take into account groundwater flow direction. The fact that statistically significant relationships were still found suggests that the results would probably not be very different if flow directions were included. However, doing so in future work would probably improve the analysis. For example the true capture zones of monitoring stations could be approximated before calculating land use densities and other variables, by using piezometric contours to estimate (even roughly) groundwater flow direction and rate. This would in turn help to delineate anisotropic (e.g. ellipsoidal) neighbourhoods based on estimated lateral transfer times.

In this respect, the case of one ‘outlier’ in the KW test with urban land use density is illustrative. This particular monitoring station was classified in the lowest urban density class, while it is one of the most contaminated wells. However, when considering groundwater flow direction and transport, other studies demonstrated that atrazine contamination of groundwater in that area was from non-agricultural origin (Debongnie et al., 1996). For that particular monitoring station, urban settings are located a few hundreds metres from the monitoring station, just outside the anisotropic neighbourhoods used in this study.

The drawback of using a one-way ANOVA in this study is the assumption that when one factor is varied in time the others remain constant (i.e. the KW test for one variable is performed independently of the other variables). This is a typical problem when data for an analysis are collected for other purposes and there is no experimental design (Worrall et al., 2002). However, the ‘one at a time’ approach of KW tests was considered to be appropriate in order to identify the important factors that explain groundwater contamination by atrazine. In the ANOVA, interactions between different factors were, therefore, not tested. In the absence of a fully designed experiment, the number of available observations per treatment combination would never be constant, and consequently the factorial analysis that could check for interactions would not be straightforward (Milton and Arnold, 2003). Future work could seek to solve this problem and thus maybe explain some of the minor contradictions that appeared for KW tests with soil properties. However, preliminary results suggest that no significant interaction term between the available factors presented here would better explain the variability of groundwater contamination. Worrall et al. (2002) successfully performed a factorial analysis on groundwater quality data, but the ANOVA was made with multiple compounds and all site properties were grouped as one treatment, while other treatments were compounds properties, between-year variability and within-year variability of pesticide concentrations.

The results found in the present study also contribute to the understanding of the dilution time for atrazine pollution in the Brusselian aquifer. Although experimental results are difficult to extrapolate to different sites, atrazine degradation in saturated conditions has most often been found to be null or very low (see the review of Hoyle and Arthur, 2000). Therefore, any decrease in atrazine concentrations is likely to result mainly from ground-

water transport and dispersion. The spatial correlation range of 600 m suggests that local point sources of pollution can affect groundwater quality on a significant distance. The order of magnitude of this correlation range is absolutely reasonable if few or no degradation occurs in the aquifer. The time series (not shown here) of some contaminated monitoring stations also indicated that pollution persistence is important in time, even after the abandonment of atrazine use. This could be related to the transfer time between the surface and the water table. With two different methods, Vanclooster et al. (2004b) evaluated the mean transfer time to be between 4 and 12 years on average for the Brusselian aquifer. Information on the horizontal transport velocity in the aquifer can be obtained from in-situ measurements (pumping tests; IBW, 1987). The complete range of hydraulic conductivity values is quite large (from 0.12 to more than 100 m.day⁻¹) due to important variations in the aquifer lithology. Assuming an effective porosity of 0.30 and a horizontal gradient of 0.01, the median horizontal transport velocity is estimated to be about 0.5 m.day⁻¹. Thus, even if all types of atrazine applications are banned from September 2005, concentrations in the aquifer will probably stay above the detection limit for several years.

4.5 Conclusions

This study used geostatistics to analyse the sources of atrazine contamination in the Brusselian sandy aquifer of central Belgium. Non-agricultural applications of atrazine ceased (in theory) from 1992 and agricultural inputs are authorised until September 2005. Apart from a particular hot spot of atrazine contamination caused by non-agricultural sources, controversy still surrounds the sources of pollution in the rest of the study area. The available data set of atrazine concentrations was used to discriminate between point and non-point sources of atrazine leaching.

Pre-processing of the monitoring data was needed because of the presence of censored data and these were treated using a simple substitution method.

The dependence of atrazine concentrations was studied in both space and time using semivariogram analyses. This gave an estimation of correlation ranges of 600 m and 600-700 days respectively and thus provided an overview of the spatial and temporal extents of groundwater contamination

by atrazine in the study area.

Furthermore, the model fits to the semivariograms were applied as declustering algorithms to the monitoring data. This corrected at least partially for the spatial dependency in the sample, so that the hypothesis of a random sample was more realistic before computing cumulative density functions and histograms and performing an analysis of variance.

Although agricultural use of atrazine is due to cease, in the present case study it was shown that the vast majority of atrazine contamination can be explained by the urban land use density and hence derives from non-agricultural sources of pollution. Furthermore, the results presented here are useful for management issues related to other chemicals, and for helping in the delineation of well protection zones. The results also confirmed that the observed pollution is expected to persist at a significant level for at least several years after the ban on atrazine inputs.