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Factors controlling spatial and temporal patterns of multiple pesticide compounds in groundwater (Hesbaye chalk aquifer, Belgium)

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Abstract

Factors governing spatial and temporal patterns of pesticide compounds (pesticides and metabolites) concentrations in chalk aquifers remain unclear due to complex flow processes and multiple sources. To uncover which factors govern pesticide compound concentrations in a chalk aquifer, we develop a methodology based on time series analyses, uni- and multivariate statistics accounting for concentrations below detection limits. The methodology is applied to long records (1996–2013) of a restricted compound (bentazone), three banned compounds (atrazine, diuron and simazine) and two metabolites (deethylatrazine (DEA) and 2,6-dichlorobenzamide (BAM)) sampled in the Hesbaye chalk aquifer in Belgium. In the confined area, all compounds had non-detects fractions >80%. By contrast, maximum concentrations exceeded EU's drinking-water standard (100 ngL⁻¹) in the unconfined area. This contrast confirms that recent recharge and polluted water did not reach the confined area, yet. Multivariate analyses based on variables representative of the hydrogeological setting revealed higher diuron and simazine concentrations in the southeast of the unconfined area, where urban activities dominate land use and where the aquifer lacks protection from a less permeable layer of hardened chalk. At individual sites, positive correlations (up to $\tau = 0.48$ for bentazone) between pesticide compound concentrations and multi-annual groundwater level fluctuations confirm occurrences of remobilization. A downward temporal trend of atrazine concentrations likely reflects decreasing use of this compound over the last 28 years. However, the lack of a break in concentrations time series and maximum concentrations of atrazine, simazine, DEA and BAM exceeding EU's standard post-ban years provide evidence of persistence. Contrasting upward trends in bentazone concentrations show that a time lag is required for restriction measures to be efficient. These results shed light on factors governing pesticide compound concentrations in chalk aquifers. The developed methodology is not restricted to chalk aquifers, it could be transposed to study other pollutants with concentrations below detection limits.

Several factors govern pesticide compounds concentrations in the chalk: hydrogeological setting, land use, groundwater level fluctuations and persistence.

1. Introduction

Groundwater pollution by pesticide compounds — pesticides and metabolites — is a worldwide environmental issue [41]. Pollution in shallow (depth < 100 m) aquifers from, among others, Asia (*e.g.* Pingali and Roger [38]), the United States of America (*e.g.* Barbash et al. [4]) and Europe (*e.g.* Loos et al. [33]), has been reported at the nano- to microgram per liter concentrations range. The concentration variability stems from several factors such as application rates, soil bio-degradation, adsorption on soil and colloids that influence pesticide transport from soil to groundwater [10]. Some pesticide compounds are more often detected (*i.e.* above detection limits) in groundwater than others. In Europe, pesticides and metabolites such as atrazine, diuron, simazine — withdrawn herbicides — and bentazone — a regulated herbicide, and deethylatrazine (DEA) occur often in groundwater (*e.g.* in Denmark [24], in France [34] and at the pan-European scale [33]).

It is critical to better understand which factors may compromise the “good” quality status of groundwater bodies hosted in chalk aquifers. The Water Framework Directive [45] and its daughter, the Groundwater Directive [13], require the “good” quality status of groundwater bodies with respect to “priority substances” that include atrazine, diuron and simazine (among others) as well as metabolites such as DEA. To comply with these directives, a status has to be assessed. As pointed out by Baran et al. [3], since observations are limited in space and time, this assessment task is challenging. This challenge may be exacerbated for groundwater bodies hosted in complex aquifer systems, such as chalk aquifers which show double-porosity flow behavior. Chalk aquifers in Western Europe host important water resources [14] — they contribute to sustain flow in sensitive ecosystems, such as rivers — and provide drinking-water, for example, in France, England [14] and Belgium [12].

There remain important unknowns regarding which factors govern pesticide compound concentrations in chalk aquifers,

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despite about two decades of studies [15, 2]. For example, dependencies between concentrations and groundwater level fluctuations are unclear: they are sometimes weak and sometimes strong in British aquifers. At Hampshire sites below a thin (31 m) unsaturated zone, 6 year long time series of isoproturon, chlortoluron and atrazine concentrations were independent of groundwater level fluctuations [10]. By contrast, in the Upper Chalk aquifer of the North Downs (UK), 5–7 years long time series of atrazine and diuron concentrations were found to be dependent on groundwater level fluctuations in a deep (36 m) well covered by a thick (31 m) unsaturated zone [28]. In the Upper Chalk, a hierarchical structure of faults and bedding plane fractures govern flow and, hence, may enhance fast transport processes [7]. Fast and slow transport processes influenced atrazine and deethylatrazine concentrations at the Trois-Fontaines spring (France), where sizes of fissures and conduit networks are less documented, but where pollutants (pesticides, nitrate and chloride) were sampled at high frequency (sub-monthly) during 13 years [2]. Precise descriptions of bedding planes or fracture networks and long time series are a pre-requisite to gain insights into which factors govern pesticide compound transport processes in the chalk, however they are still rarely available. It is still not known whether pesticide compounds occur frequently in chalk aquifers from Belgium. If they do, factors governing their occurrence in groundwater are not yet known.

Pesticide compound concentrations are often reported below the analytical detection limit (non-detects), these non-detects require appropriate statistical methods. Non-detects are sometimes discarded or imputed by half of the detection limit or by zero (*e.g.* Köck-Schulmeyer et al. [26] and Baran et al. [2]). But, discarding or imputing non-detects might bias summary statistics [22], such as mean or median concentrations — used to assess the quality status of a groundwater body. When non-detects were not included in the analysis, Hansen et al. [21] showed that median bentazone and glyphosate concentrations in Danish groundwaters were over-estimated — up to a factor 100 000. More realistic statistics can be computed using methods, such as the “robust” regression on order statistics (ROS), which account for non-detects [22]. In the ROS method, a regression model is applied to a probability plot of measured concentrations and theoretical probability distributions to impute censored values [22]. Vonberg et al. [44] compared mean concentrations of atrazine at local sites (wells) after imputing non-detects by arbitrary values and ROS ; these authors found more realistic mean estimates with ROS imputed data. Hansen et al. [21] and Vonberg et al. [44] pointed out that evaluating country and aquifer wide (respectively) state of pollution remained uncertain — even using non-detects — because of changes in sampling frequency: less polluted sites tend to be less frequently sampled.

Groundwater dating and quality (linked to pollution) may be tightly linked because of effects of anthropogenic activities. Groundwater dating consists in determining an aver-

age age and a distribution of residence times of groundwater in aquifers, it is based on concentrations of natural or “anthropogenic” age tracers found in ground-waters, such as tritium (see Phillips and Castro [37] for an overview). Interpreting tracer concentrations is not trivial because heterogeneous permeability distributions induce complex flow-paths, that give various travel times. Thus, a water sample provides an average age from a mix of flow lines [6]. Mixing of older and younger ground-waters can lead to biased estimates of mean groundwater age (*e.g.* Solomon and Sudicky [42]). Age variability depends, in part, on the depth of the sampled well. The variability can be constrained by sampling age tracers from multi-level sampling wells, which intersect different flow lines. Despite these limitations, age tracers can relate to the vulnerability of aquifer systems because they often enter groundwater at the same time of pollutants, during recharge. Older groundwater may be better protected and less vulnerable to pollution than modern groundwater which are found in recharge zones, where pollutant infiltration can occur.

The aim of this paper is twofold. (1) To describe a methodology that combines hydrogeological, uni- and multivariate statistical tools to analyze the spatial distribution and time trends of pesticide compounds having concentrations below detection limits in groundwater. (2) To contribute to expand the knowledge on pesticide content in chalk aquifers by presenting results from a 18-year monitoring program carried out in an Belgian aquifer subject to substantial agricultural pressure.

2. Methods

2.1. Study site characteristics

The Geer catchment is located 15 km northwest of Liège in Belgium (Figure 1 a.). The catchment covers 480km² at a mean altitude of 140m above sea level. Agriculture dominates land use: it covers 80 % of the area. Crops are mainly cereals (wheat, barley and flax) and sugar beets [23]. The remaining 20% of the area are divided between forest (7%) and urban activities — including industries it covers 13%. These urban activities are the densest to the southeast of the basin, as proved by dense transportation networks (Figure 2 a.).

Fertilizer use in agriculture and — to a lesser extent — waste water leakage in urban areas, degrade groundwater quality in the Hesbaye chalk aquifer underlying the Geer catchment [9, 36, 20]. Nitrate concentrations in groundwater increase with an average slope of 37% per year [5]. This increase threatens the local groundwater resource which provides large volumes (about $30 \times 10^6 \text{ m}^3 \text{ y}^{-1}$) of drinking-water to inhabitants of Liège and its suburbs [8].

The chalk aquifer dips ($\sim 1\text{--}2^\circ$) toward the north and is made of four main hydrogeological units (Figure 1). These units consist of the following lithology (top to bottom):

1. Quaternary loess deposits (5–20m thick) constitute the unsaturated zone and regulate the aquifer recharge;

2. Flint conglomerate (2–10m thick) that results from past chalk dissolution and alteration;
3. Maastrichtian (10–15m) and Senonian (20–40m) fractured chalk layers that constitute the aquifer; a discontinuous intermediate layer of hardened chalk (1–2m) with low permeability separates both chalk layers;
4. Campanian smectite marls constitute the impervious base of the aquifer.

The chalk aquifer is divided between an unconfined and a confined area. An unconfined area implies that recharge occurs where the water can percolate through the thick unsaturated zone — in the 10–~40 m range —, to the south of the Geer river. In a confined area, an impervious layer impedes recharge from the surface or adjacent aquifers. The regional groundwater flow is from south to north (Figure 1 b.). Discharge occurs southeast of the confined area, the Geer river drains the aquifer from west to east. Groundwater level fluctuations follow multi-annual cycles with large amplitudes (>12 m) occurring where boundary conditions (Geer river or groundwater divide) effects are low, i.e. at the center of the unconfined area [9, 20].

2.2. Pesticide data, monitoring network and tritium data

Table 1 presents properties of the compounds, details on supposed introduction year, ban date in Belgium and Groundwater Ubiquity Scores (GUS) [18]. These scores are based on soil half-life and partition coefficient between soil organic carbon and water. GUS helps characterize the degree to which pesticides may leach. Leachability is divided in three classes: low for $GUS < 1.8$, transition-state for $1.8 > GUS > 2.8$ and high for $GUS > 2.8$ [18]. Data on the chemical composition — pesticide compounds and nitrate (NO_3^-) — of the Hesbaye chalk were sourced from water quality databases of the Walloon region (SPW-DGO3) and private water companies. The data set spanned the January 1996–January 2014 (1996–2013) time period, covering almost 20 years. Datasets were taken from 22 abstraction sites (Figure 2 a.) which, except for 3 underground galleries (8, 10 and 11), are abstraction wells. In these wells, except at 5 sites (18–22), the screen’s length is unknown but presumably complete. Thus, water samples represent a mix of flow-paths with different age.

Complementary information including groundwater elevations, water level time series and tritium content were compiled from the literature and online sources. Water elevations were sourced from the last exhaustive survey (235 measurements in 2008 [40]). Differences between water elevations and well altitudes were used to estimate the unsaturated zone thickness at each site. Similarly, differences between well depth and water level elevation were used to estimate well water columns. Groundwater level time series, with typical multi-annual fluctuations were sourced from the database of the Walloon region¹. Tritium (^3H) concentrations from

16 sites were sourced from a survey performed in 2005 to characterize and model NO_3^- transfers in the Hesbaye chalk, sampling and analysis details are provided by Orban et al. [36]. ^3H is a water age tracer linked to anthropogenic activities — thermonuclear bomb tests starting in 1953 and during the 1960’s created an artificial ^3H peak in rainfall that transferred to groundwater, this tracer is used to determine residence times. Old groundwater is defined relative to the 1953 threshold year and corresponds to $^3\text{H} < 2\text{TU}$.

2.3. Statistical analyses

2.3.1. Non-detects

Pesticide compound concentrations were reported below detection limit ($< 10 \text{ ngL}^{-1}$), these values (non-detects) make the data “left-censored” and require appropriate methods to assess spatial and temporal trends. Non-detects were included in the pairwise correlations: a preliminary analysis used for the spatial distribution in the unconfined area and an exploration of dependencies with groundwater level fluctuations. Furthermore, non-detects were used to compute summary statistics (mean, median and quartiles) on four kinds of samples: (1) with all data available for the whole aquifer system (confined and unconfined areas), (2) for the unconfined area only, (3) for each site and (4), for each year by aggregating data from the unconfined area. For all these analyses, non-detects were not imputed by half of the detection limit as often done in previous work. Summary statistics were estimated based on the “robust” regression on order statistics (ROS) method, which is appropriate for non-detects fractions $< 75\%$ [22] and for concentration time series observed at each site. As in Hansen et al. [21] we assumed that pesticides concentrations and non-detects were log-normally distributed. The log-normal distribution often describes water quality data sets [22]. These analyses used NADA [31] in R.

2.3.2. Spatial analyses

Preliminary spatial analyses used pairwise correlations with the non-parametric Kendall’s τ coefficient [25]. This coefficient provides a measure of monotonic correlation between two variables, censored or not. Significance was determined at $p\text{-value} < 0.05$ and corrected with the Bonferroni correction.

The spatial distribution of pesticide compound concentrations in the unconfined area was interpreted with a clustering based on hydrogeological variables. Specifically, the clustering was based on a principal component analysis (PCA) of five hydrogeological variables (means) for each site: longitude, latitude, unsaturated zone thickness, well water column and tritium concentration. For the PCA analysis, variables were checked for normality (log-transformed when required) and they were scaled, because they had different units (*e.g.* ^3H (TU) and longitude (m)). The principal components were used for hierarchical clustering: the individuals’ coordinates on principal components was used to classify and group individuals homogeneously. The number of clusters was de-

¹Piez’eau. Accessible at: <http://piezo.environnement.wallonie.be/>

terminated with the optimal inertial gain criteria and checked visually; it uses the Ward algorithm, which maximizes inter-class inertia to obtain compact spherical clusters. Last, pollutant's means estimated at each site with the ROS method were projected on the principal components, as supplementary variables and they were tested (v-tests) for dependence with axes. These analyses used FactoMineR [30] in R.

2.3.3. Temporal analyses

Concentration time series were searched for dependencies with groundwater level fluctuations and for temporal trends. To match the shortest sampling time interval between two pesticide compounds concentrations, NO_3^- concentrations and groundwater levels time series were converted to monthly averages. Monthly averages cannot describe "fast transfer" processes expected for rainfall events occurring at daily time scales. However, the effect of these events is deemed negligible for the Hesbaye chalk aquifer, because the thick unsaturated zone buffers transport processes and induce transfers over longer time periods (month or years).

Dependencies between groundwater level fluctuations and pesticide compounds concentrations were estimated on a site by site basis using pairwise correlation using Kendall's Tau, as described above. Differently, temporal trends in annual mean and median concentrations were explored by aggregating — by year — all observations from the unconfined area. When a significant trend was determined, the trend slope was estimated with the Theil-Sen slope estimator. For both methods, significance was determined at $p\text{-value} < 0.05$.

3. Results and analyses

This section explores factors governing pesticide compound concentrations in the Hesbaye chalk aquifer. The first three sections focus on spatial factors: the concealment nature of the aquifer, hydrogeological and land use settings. The last two sections focus on temporal factors: groundwater level fluctuations and trends for the most polluted part of the aquifer — the unconfined area.

3.1. Regional spatial analyses

3.1.1. Summary statistics and detection frequencies in the Hesbaye chalk aquifer

Surface applications of atrazine, bentazone, diuron and simazine and their metabolites deethylatrazine (DEA) and 2,6-dichlorobenzamide (BAM) pollute the Hesbaye chalk groundwater. Pesticide compounds (and nitrate – NO_3^-) spanned a broad range of concentrations in groundwater (Figure 3). Median concentrations of pesticides and metabolites and NO_3^- are below their respective EU's drinking-water standards of 100 ngL^{-1} and 50 mgL^{-1} (Figure 3 a.). By contrast, maximum concentrations exceeded the standard, both for banned and restricted compounds. Non-detects fractions were unevenly distributed between the confined and unconfined areas of the aquifer — fractions $\geq 70\%$ in the confined

area (Figure 3 b.). Below, we identify the nature of this uneven distribution and the role played by the concealing clay layer of the northern part of the aquifer.

3.1.2. Effects of aquifer concealment and residence time on pesticide pollution in the Hesbaye chalk aquifer

To explore how pesticide compound concentrations depend on the concealment of the aquifer we compared, between confined and unconfined sites, maximum pollutant concentrations and fractions of non-detects to tritium (^3H) content, a marker of groundwater residence times. Sites in the confined area had very high fractions of non-detects (80% see Figure Appendix .1) and low ^3H concentrations ($\leq 2\text{TU}$), suggesting pristine groundwater with long residence times. In other words, groundwater residence times from the confined area seems longer than pesticide transfer time. In the confined area, groundwater is unpolluted, to date. A contrasting situation occurs in the unconfined area where pollutants reached maximum concentrations. For instance, Site 9 had an atrazine concentration of 219 ngL^{-1} , Site 4 had a bentazone concentration of 149 ngL^{-1} and Site 13 had a simazine concentration of 347 ngL^{-1} concentrations; Site 14 had a 2,6-dichlorobenzamide concentration of 502 ngL^{-1} and site 7 had a deethylatrazine concentration of 167 ngL^{-1} . Furthermore, most fractions of non-detects are $\leq 50\%$ and ^3H contents were in the $\geq 2\text{--}15\text{TU}$ range, indicating a mix of short and long residence times. Because it is subject to recent recharge, the unconfined area has its groundwater polluted by pesticide compounds.

A plausible reason for the contrasting states of pollution found between the confined and unconfined areas is the aquifer's partial cover by the Tertiary clay layer. Assuming that pesticides (and ^3H) were uniformly spread in space, some amounts of pollutants and ^3H would be found in the groundwater from the confined area, if the clay layer was leaking. Such hypothesis is contradicted by the lack of pollutants and ^3H in the confined groundwater. So, the clay layer impedes downward vertical transfers of modern water and pollutants to the confined groundwater. The uniform spreading assumption is strong, because pesticide applications may have varied in space and time. Unfortunately these variations are not yet documented but agriculture dominates land use over both confined and unconfined areas (Figure Appendix .2). The nature of the combined lack of pollutants and tritium corroborates previous findings that focused on NO_3^- pollution only [20, 36].

Although the confined area is protected from downward transfers, some lateral transfers may introduce recent groundwater and pollute the pristine confined groundwater. Lateral transfers likely occur at sites close to confined/unconfined interface. For instance, the pumping Site 19 had ^3H contents $>2\text{TU}$ and an atrazine non-detect fraction of $\sim 80\%$ (Figure Appendix .1). At the confined/unconfined interface, pumping sites may enhance lateral flow from the unconfined to the confined area and attract modern groundwater and pol-

lutants. More generally, the lateral flow process complements others processes (*i.e.* rapid flow pathways through windows, long-term artificial recharge and rapid pathways in the saturated zone) postulated by Lapworth et al. [27] to explain occurrences of micro-organic pollutants that increase pollution in confined chalks. To sum up, we confirmed that an impervious clay layer acts as a hydraulic barrier that protects a confined area from downward vertical pollutant transfers; but despite such protection, lateral flow processes could bring water polluted because it infiltrated in the unprotected recharge area.

Comparing pollutant concentrations between shallow (depth ≤ 35 m) and deep sites revealed lower concentrations at deep sites (Figure Appendix .3), which would be inline with groundwater stratification. Groundwater stratification may explain the vertical distribution of pesticide compounds in the unconfined area. In a sandy aquifer, Baran et al. [3] and Gutierrez and Baran [19] showed along a depth gradient that the older the groundwater, the lower the atrazine concentrations. Identifying groundwater stratification in the Hesbaye chalk is uncertain, because most wells are fully screened. For instance, low ^3H content were concomitant to maximum diuron and simazine concentrations at Site 13 — from the up-gradient recharge area. By contrast, low ^3H content and high (>80%) non-detect fractions for most pollutants were found at Site 22 — the deepest site in the discharge area. Reduced uncertainties required to test this hypothesis may be reached with samples collected from multi-level well clusters (*e.g.* Baran et al. [3]), it shall be investigated in future work.

3.1.3. Effects of hydrogeological setting and land use on concentrations in the unconfined area

Explaining effects of the hydrogeological and land use settings on pesticide compound concentrations is a challenging task, especially at a regional scale. To address this challenge, a preliminary exploration of dependencies among pollutants was performed to unravel any spatial pattern. One high ($\tau = 0.62$) and three medium positive dependencies ($0.42 < \tau < 0.49$) were found (Figure Appendix .4): atrazine–deethylatrazine and NO_3^- –atrazine, NO_3^- –deethylatrazine, and atrazine–simazine, respectively. These dependencies suggest similar sources and modes of transport — such as diffuse agricultural sources and transport as solutes. However, most dependencies were weak or not significant. This result is not a surprise, because NO_3^- and pesticides can have different periods of application, cycle of transformation and remobilization and modes of transport, such as with colloids. Under colloidal transport, pesticide compounds occurrences in chalk groundwater are influenced by the unsaturated zone thickness. Empirical results from Gooddy et al. [16] show that colloids and diuron get trapped when transported through a thick unsaturated zone and that only diuron as a solute occurs in groundwater. The correlation approach provides an overview of global dependencies but it is limited, an other method which accounts for relevant factors is explained be-

low.

To analyze effects of multiple factors on the spatial distribution of pesticide compound concentrations in the unconfined area of the Hesbaye chalk aquifer, we used a spatial partition methodology based on groups of sites with similar hydrogeological variables. In the principal component analysis (PCA), the first two principal components (PCs) justified together 83% of the variance (Figure 4). In PC1, latitude ($r=0.96$), longitude ($r=0.61$) anti-correlated to the ^3H ($r=-0.81$). These results agree with increasing groundwater residence times along the south–north regional flow direction. In PC2, the unsaturated zone thickness ($r=0.79$) and longitude ($r=0.69$) anti-correlated to the well water column at each site ($r=-0.86$). These results agree with a gradual increase of depths to the groundwater from north to southwest in the unconfined area (Figure 1). Thus, these first two PCs provide results consistent with the conceptual hydrogeological model of the unconfined area; and, they help to reduce dimensionality before applying hierarchical clustering.

Hierarchical clustering resulted in four groups (Gp.1–4) of sites that illustrate a spatial distribution consistent with the hydrogeological setting of the unconfined area (Figure 4). Orban et al. [36] divided this area in two groups on the basis of ^3H and NO_3^- concentrations only. One finds two similar groups by considering Gp.4 and merging Gp.1–3. Our clustering provides alternative groups for the area since it includes others factors. Although the multivariate analyzes allow identifying effects of land use differences and hydrological setting on pollutant concentrations, they remain limited because, yet, they do not account for possible spatial and temporal changes of application rates of pesticides. These changes may be characterized by conducting farmers interviews, as was done for instance by Amalric et al. [1]) for a 4km^2 basin. These efforts were out of the scope of this study which focus on a 480km^2 basin.

To interpret the spatial distribution of pesticide compound concentrations we projected pesticide compounds concentrations on the PCA and related the projection to the clustering. The three compounds diuron, simazine and BAM (Figure 4, top) had positive dependencies with the second principal component. Clustering results provide which group corresponds to the projection of the three pollutants — here, Gp.2 (Figure 4, bottom). Gp.2 contained sites from the southeast of the unconfined area. There, urban and industrial activities are the densest (Figure 4, right). These activities may explain the concomitant occurrence of these three compounds in groundwater. Indeed, diuron, simazine and dichlobenil (BAM's parent compound) have been used for weed control on highways, rail tracks and public or private amenities — among others — in Belgium [35]. Two observations further supports this interpretation: (1) the weak correlation between diuron and atrazine (Figure Appendix .4) and (2) the relatively higher diuron, simazine and BAM concentrations of Gp.2 v. the three other groups (Figure Appendix .5). The latter groups had concentrations of the two herbicides used for agriculture pur-

poses, atrazine and bentazone, higher than in Gp 2; this result confirms the dominating pressure of agriculture on groundwater’s quality in the unconfined area. A similar contrast of pesticide compounds occurrence between urban/industrial and agricultural areas was reported by Sørensen et al. [43]. Our results confirm a similar case where diuron concentrations occurred such as: industrial > urban > arable in the Lewes Nodular Chalk Formation (UK) [29].

We conclude this section by a complementary discussion on land use, preferential pathways and the unsaturated zone. In the southeast of the unconfined area, the combination of land use and the hydrogeological setting induce pollution by the two pesticides of transition-state leachability: diuron and simazine. In this area, previous studies (*e.g.* Battle-Aguilar et al. [5] and Hallet [20]) reported early pollution and upward trends (slope up to 47% per year) of NO_3^- caused by a combined effect of flow through preferential flow pathways and the lack of protection provided by the hardened intra-bed chalk layer of low permeability (hardground). Again, hierarchical flow through bedding plane fractures can enhance direct infiltration and influence pollutant transport [7]. The high density of roadways can favor preferential pathways for the transport of pesticide compounds to groundwater, for instance soak-ways can by-pass flow through the soil and part of the unsaturated zone [15, 10]. However, direct infiltration is debatable for chalk aquifers covered by thick unsaturated porous layers, such as glacial deposits in Denmark or loess Belgium, because these layers can regulate pollutant infiltration by controlling downward fluxes [9] and by trapping pollutants, dissolved or associated to colloidal transport [16].

3.2. Temporal analyses in the unconfined chalk

3.2.1. Effects of water table fluctuations on concentrations at individual sites

Groundwater level fluctuations may enhance atrazine concentrations via remobilization processes from the vadose zone in chalk [28] and sand aquifers [3]. Sites from the unconfined area had atrazine, BAM, bentazone, DEA, diuron, simazine and NO_3^- concentrations positively correlated ($0.24 < \tau < 0.71$) to multi-annual groundwater level fluctuations (Figure 6). These results confirm the hypothesis of remobilization processes for pesticide compounds and NO_3^- . NO_3^- remobilization was previously suggested by Orban et al. [36], Brouyère et al. [9], Hallet [20]. Pollutants (pesticides and NO_3^-) are transported downward through the unsaturated zone and leach when the groundwater level rise during multi-annual fluctuations. Thus, groundwater level rise and fall increase and decrease respectively the local groundwater pollution state.

Well depth and leachability may favor correlations between pesticide compound concentrations and groundwater level fluctuations. A preferential remobilization of pesticide compounds was found at shallow sites in a semi-confined chalk aquifer with thick (30 m) unsaturated zone [28]. Assuming a depth threshold of 30 m — shallow ≤ 30 m and deep > 30 m —

only Site 2 (among 4 shallow sites) had pesticide compounds correlated to groundwater level fluctuations (Figure 6). This result contrasts with the hypothesis of preferential remobilization. This contrast can be explained by overlying sands and other deposits which provide a relative protection to the unique — deep — site not having any correlation as discussed in Lapworth and Gooddy [28]. As showed above, where a clay layer protects the Hesbaye chalk from modern recharge (confined area), groundwater is pristine. Yet, a preferential remobilization process cannot be identified for pollutants found at shallow unconfined sites.

To unravel a pattern of correlations between groundwater level fluctuations and pollutant concentrations dependent on leachability, we ordered correlation results by groundwater ubiquity score (GUS). Correlations depended on GUS: the larger the GUS, the larger the number of correlated sites. Specifically, transition-state GUS pesticides — diuron and simazine — correlated once and none respectively but, high GUS compounds — atrazine, bentazone and DEA — correlated at three sites. For instance at Site 6, high GUS compounds had correlations in the $0.36 \leq \tau \leq 0.58$ range. These results confirm the hypothesis that leachability, assessed by considering sorption and degradation processes in soil, could explain, at least at some sites, differences in correlation between pesticide compounds and groundwater level fluctuations in the Hesbaye chalk. To conclude, pollutant remobilization is expected in the future, because it depends on hydrological variability and, as we shall see below, persistence.

3.2.2. Trends and persistence of pesticide compounds in the unconfined chalk

To assess if good land use practices, such as the ban of a compound, are efficient we characterized temporal trends of pollutant concentrations. This characterization was performed with help of boxplots showing mean and median annual concentrations of banned and currently restricted pesticide compounds (Figure 5). We observed annual concentrations of atrazine, bentazone and DEA — used in agriculture areas — higher than simazine and diuron concentrations — used in urban and industrial areas. This observation is in line with agriculture dominating land use in the Geer basin.

Differences in ban date can affect the use of pesticides at the scale of the unconfined area and can affect the temporal evolution of concentrations. Banned triazines (atrazine, simazine and DEA) and regulated bentazone showed opposite trends in annual concentrations (Figure 5). Specifically, median concentrations of atrazine ($\tau = -0.69$), simazine ($\tau = -0.61$), DEA ($\tau = -0.48$) and BAM ($\tau = -0.55$) had negative correlations with time. By contrast, bentazone’s median concentrations had a positive correlation ($\tau = 0.52$). These contrasting trends could lead to the following interpretation: bentazone use increased to replace triazine compounds post ban year. But, it is not the case. Decreasing annual triazine concentrations may be explained by long-term use reductions, which relate to decreasing sold volumes since the mid-1980s

(Figure Appendix .6). After atrazine's ban in 2004, bentazone sales remained constant. Constant sales contradicts a replacement hypothesis. To explain upward bentazone trends, we noticed that bentazone sales were fluctuating: sales increased between 1980-1991 and 2000-2004 and dropped in 2007, because of restriction measures. Either increase indicate more applied volumes, which can affect bentazone's concentrations and explain the increasing trend. The number of studies on bentazone concentrations trends in chalk aquifers are yet limited. Lapworth et al. [29] studied bentazone fluctuations during 22 months and found that local increasing (not quantified) trends depended on recharge fluxes. On the basis of >18 year long time series, Hansen et al. [21] estimated an upward trend of bentazone concentrations in all Danish groundwater bodies — with chalk aquifers. Therefore, our findings corroborate the increasing bentazone trends reported by Lapworth et al. [29] and Hansen et al. [21]. It must be acknowledged, however, that comparing slope trends between aquifers is uncertain. In particular because, the hydrogeological setting and land use can influence transport processes or because sampling strategies sometimes shift toward more frequent monitoring of "high risk groundwater". Applied to NO_3^- concentrations, a pollutant free from changes in sampling strategies, our method proved robust: the 39% slope estimated for mean annual concentrations is close to the 37% of Batlle-Aguilar et al. [5].

The lack of break in pollutant concentrations time series and some annual maximum exceeding EU's standard post ban year are evocative of persistence. Persistence is an issue for water bodies, such as the Hesbaye aquifer, used for drinking water supply. Atrazine is the longest banned compounds of this study (Table 1) and results suggested a lag time of at least eight years for this compound (Figure 5). A time lag is required for policy-driven use reductions to be efficient. A similar lag in atrazine concentrations was reported by Gutierrez and Baran [19] for a 4 km² French catchment. A reason for delayed responses is persistence effects. Triazine compounds (atrazine and simazine) can persist in chalk groundwater, as reported for instance in Lapworth and Gooddy [28]. Some differences in trapping in the unsaturated zone can combine with persistence. For instance, diuron concentrations did not have a significant trend and were lower than atrazine's probably because a fraction related to colloidal transport was trapped. Last, the slow vertical motion of ($\sim 1 \text{ my}^{-1}$ [9, 36]) solutes in the unsaturated zone may act as a temporary storage zone. A slow migration is inline with remobilization processes argued above. Further insights on unsaturated zone transfers could be gained with vertical concentrations profiles, these are not yet available.

We now turn to maximum concentrations exceeding EU's standards. These maxima seem affected by the pollutant's leaching properties. Pollutants with high leachability (high Groundwater Ubiquity Score (GUS)) exceeded EU's standard annually — for instance, atrazine concentrations do since 2008 (Figure 5). By contrast, maximum concentrations for

pesticides of lower leachability — transition-state GUS — exceeded the standard episodically — twice and four times for diuron and simazine respectively. Again, the thickness of the unsaturated zone may affect the form (colloidal, solute or both) under which these pollutants are transported to and found in groundwater.

Differing transport properties between parent compound and degradation products can alter rates of transport and/or fate [17]. BAM concentrations were higher than its parent compound, dichlobenil was never detected over the observation period (data not shown). This observation supports assumption of differing transport rate and is likely linked to BAM's GUS, which is higher than dichlobenil's (7.35 vs 2.25). BAM is prone to leach whereas its parent is not [39]. In addition, the degradation of BAM is low in saturated chalk, which makes it persistent [11].

To sum up, an almost instantaneous ban of pesticide use does not result in an instantaneous decrease of pesticide compound concentrations in groundwater from the Hesbaye chalk aquifer. Trends and maximum concentrations exceeding EU's standard show that the "good" quality status the Hesbaye chalk must reach to comply with the Water Framework Directive is compromised by pesticide use — banned or not.

4. Conclusions

This study was a two-fold contribution. It aimed at (1) developing a methodology to analyze which factors govern the spatial and temporal occurrence of pesticide compounds in groundwater and (2) contributing to expand the knowledge on pesticide content in chalk aquifers with results from a Belgian aquifer. The methodology was based on uni- and multivariate statistics which accounted for concentrations below detection limits and relevant hydrogeological factors. The study presented, for the first time, results from a long monitoring program (1996-2013) conducted in the Hesbaye chalk aquifer in Belgium which focused on four pesticides (atrazine, bentazone, diuron and simazine) and two metabolites of withdrawn active substances (deethylatrazine (DEA) and 2,6-dichlorobenzamide (BAM)).

Including non-detects in our analyses allowed to provide less biased estimates of mean and median concentrations to characterize the spatial distribution and the temporal evolution of pollutants in the aquifer. Regarding the spatial analysis, the methodology allowed to explore effects of hydrogeological and land use settings. Regarding the temporal analyses, the methodology allowed to explore effects of multi-annual groundwater level fluctuations and trends on/of pesticide concentrations in the unconfined area.

The principal outcomes for the study site are:

- Aquifer concealment and a lack of recent recharge (that is, after 1953) explain the lack of pesticide compounds in the confined area of the Hesbaye chalk.

- The hydrogeological and land use settings explain the variability of the spatial distribution of pesticide compound concentrations in the unconfined area of the chalk.
- A remobilization process of pollutants results from multi-annual groundwater level fluctuations. This process affects all pesticide compounds and preferentially those having high groundwater ubiquity scores: atrazine, bentazone, DEA and BAM.
- Persistence and downward transfer (with relatively slow velocities) through the unsaturated zone induce continuous or episodic maximum concentrations exceedance of EU's drinking-water standard, which are issues for drinking water supply.
- Contrasting trends among pesticide compounds used for agricultural purposes were identified and related to the aquifer's long time responses (>20 years) to surface good practice measures.

These outcomes shed light on spatial and temporal factors governing pesticide compound concentrations in the Hesbaye chalk aquifer in Belgium. More generally, the methodology proposed herein could be transposed to study transport of pollutants having concentrations below detection limits, such as emerging contaminants, in other aquifers (chalky or not).

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Tables and Figures

Table 1: Physical properties and ban date of the pesticide compounds from this study. DEA, deethylatrazine; BAM, 2,6-dichlorobenzamide; GUS, Groundwater Ubiquity Score [18]; restr. 2007, restricted use since 2007.

^a Data from the Pesticide Properties DataBase [32].

^b Dichlobenil (BAM's parent compound) was used on amenities, banned since 06/2009–03/2010 in Belgium.

Substances	Class	Introduction ^b	Ban date	GUS ^a	Soil 1/2 life (d)	H ₂ O Sol. (mg.L ⁻¹)	Sorp. coef. K _{oc} (L.kg ⁻¹)	Main Usage
BAM ^b	Metab.	-	-	7.35	73-173	1830	-	*Urban
DEA	Metab.	-	-	4.37	45-170	2700	110	
Atrazine	Herbicide	1957	09/2004-5	3.2	6-108	35	100	Arable agriculture
Bentazone	Herbicide	1972	restr. 2007	2.89	4-21	570	55.3	Arable agriculture
Simazine	Herbicide	1960	12/2007	2.00	27-102	5	130	Urban, railways
Diuron	Herbicide	1951	12/2007	1.83	20-231	35.6	813	Urban, railways

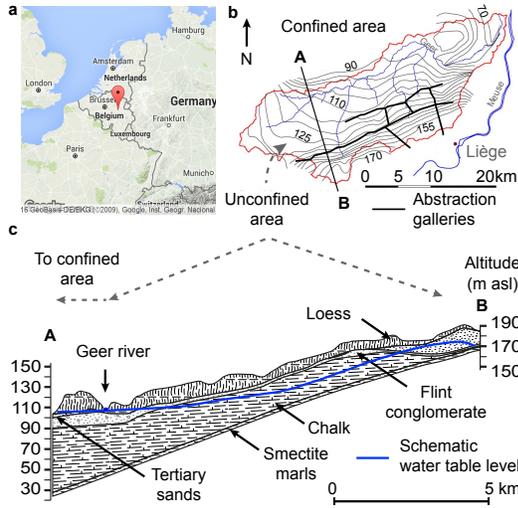


Figure 1: General localization and hydrogeological setting of the Hesbaye chalk aquifer in Belgium. **a** Geographical location. **b** Piezometric map with contour level every 5 m from a survey conducted in low groundwater level (August 2008 with 235 measurements) and cross-section location (AB line) in the unconfined area of the chalk aquifer (modified after Rothy and Dassargues [40]). **c** Schematic cross-section of the aquifer (modified after Brouyère et al. [9] and Hallet [20]). The regional groundwater flow is oriented from south-southwest to north-northeast in the unconfined area of the Hesbaye chalk aquifer.

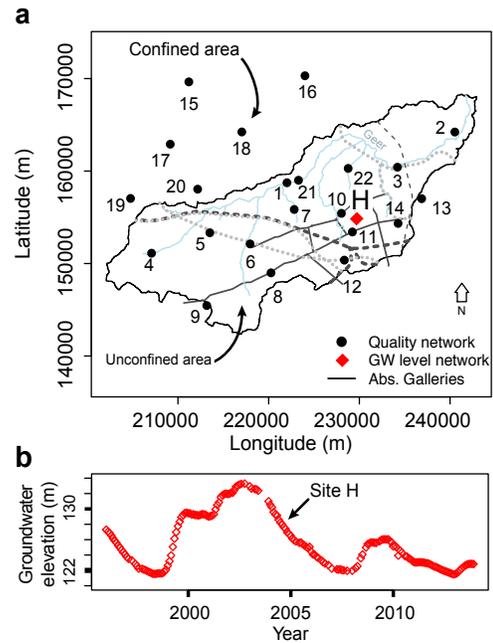


Figure 2: Map of observation sites and groundwater level time series in the Hesbaye chalk. **a**, Localization of the 22 sites used in this study with pesticide compound records (black dots) and 2 sites for groundwater levels monitoring (blue and red dots). Limits of the unconfined area are in black. Dashed black and grey lines are highways and railways respectively (coordinates in Belgian Lambert 1972). **b**, Multi-annual water level fluctuations dominate the cycle of high and low groundwater levels in the Hesbaye chalk. Top: month-average groundwater fluctuations of low (Site L – blue) and high (Site H – red) amplitudes; bottom: scaled groundwater level fluctuations.

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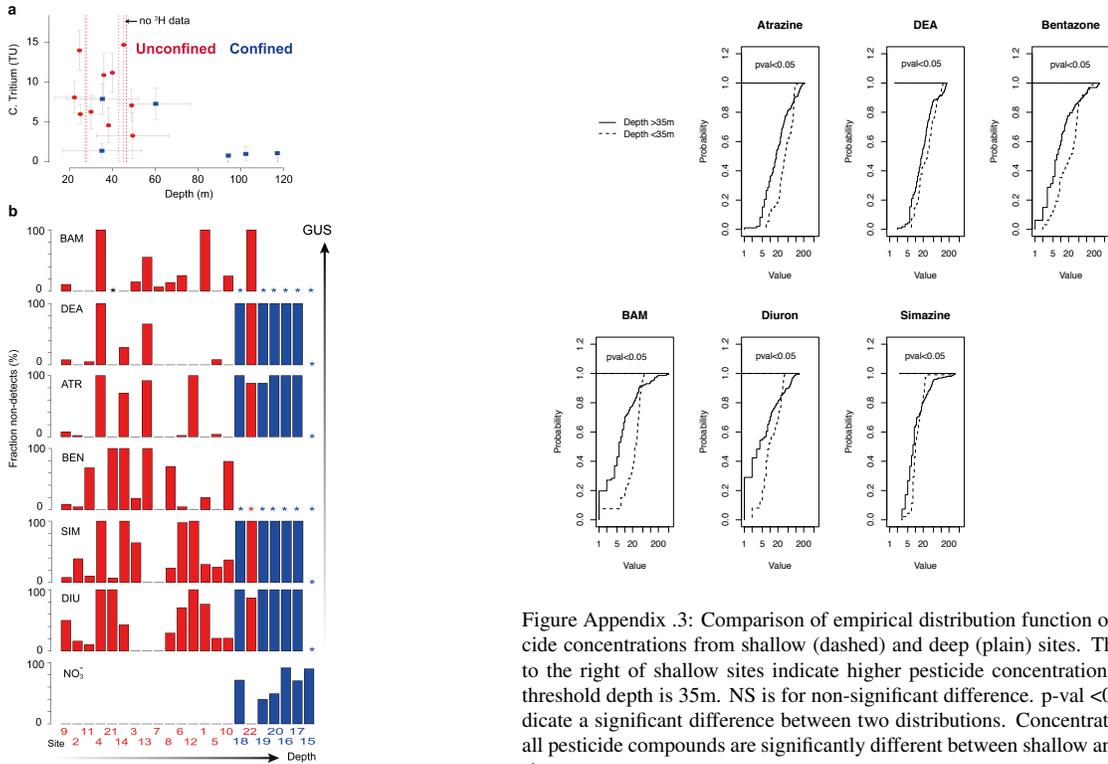


Figure Appendix .3: Comparison of empirical distribution function of pesticide concentrations from shallow (dashed) and deep (plain) sites. The shift to the right of shallow sites indicate higher pesticide concentrations. The threshold depth is 35m. NS is for non-significant difference. p-val <0.05 indicate a significant difference between two distributions. Concentrations of all pesticide compounds are significantly different between shallow and deep sites.

Figure Appendix .1: Tritium concentrations and fractions of non-detects for pesticide compounds at sites from the confined (blue) and unconfined (red) areas. **a**, Tritium concentrations from the unconfined and confined area versus depth. Vertical grey bars show the uncertainty in tritium concentration and vertical (blue) dashed bar are censored concentrations. Horizontal bars indicate known limits of top and bottom well's screen. **b**, Fraction of non-detects for 2,6-dichlorobenzamide (BAM), deethylatrazine (DEA), atrazine (ATR), bentazone (BEN), simazine (SIM), diuron (DIU) and NO_3^- at all sites from the Hesbaye chalk. * indicate no value available. Sites from the confined area have the highest non-detects fractions.

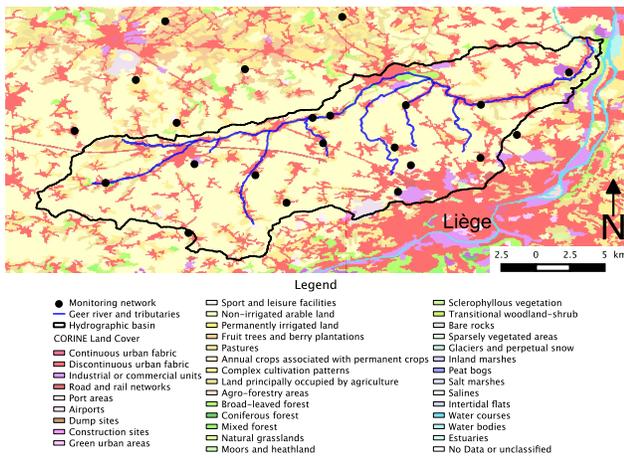


Figure Appendix .2: Agriculture dominates land use over the unconfined (hydrographic basin) and confined (to the north of the basin) area as shown from the dominating yellow colors of the CORINE Land color palette (data available at: <http://www.eea.europa.eu/data-and-maps/data/clc-2006-raster-4>).

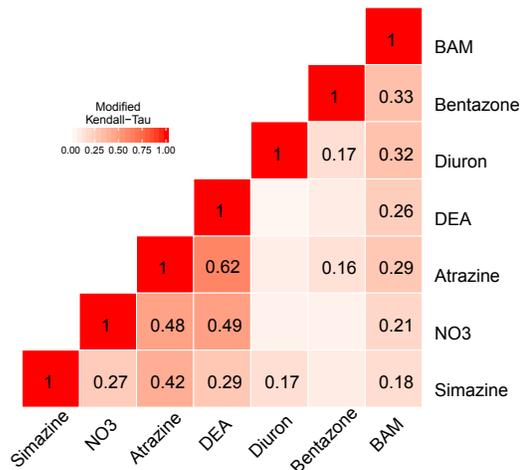


Figure Appendix .4: Correlation matrix (p-value <0.05) between pesticides, metabolites and NO_3^- at sites from the unconfined area of the Hesbaye chalk. Atrazine and its metabolite deethylatrazine (DEA) have the highest correlation.

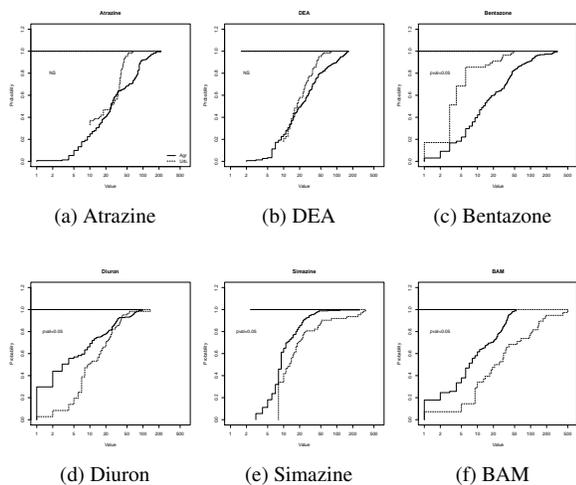


Figure Appendix .5: Comparison of empirical distribution functions and differences for each pesticide compounds considered in this study between Gp.2 (dashed lines) v. all other (GP.1, 3 and 4 – plain lines). Diuron, simazine and BAM have significant differences (p-val <0.05). For these three compounds, the shift to the right of the empirical distribution function indicate higher concentrations, which relate to the use of these compounds in urban areas.

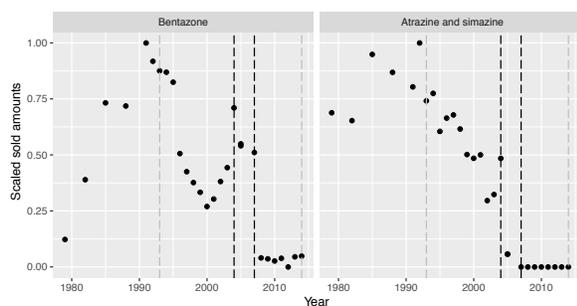


Figure Appendix .6: Scaled time series of bentazone and triazine (atrazine and simazine) volumes sold in Belgium. Vertical grey dashed lines indicate start (1996) and end (2013) years for pollutant time series from this study. Vertical black dashed lines indicate ban year for atrazine (2004) and the respective ban and restriction year (2007) for simazine and bentazone. Data from Belgian Federal Public Service Health, Food Chain Safety and Environment.