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Åkesson, Maria; Sparrenbom, Charlotte; Christel, Carlsson; Jenny, Kreuger

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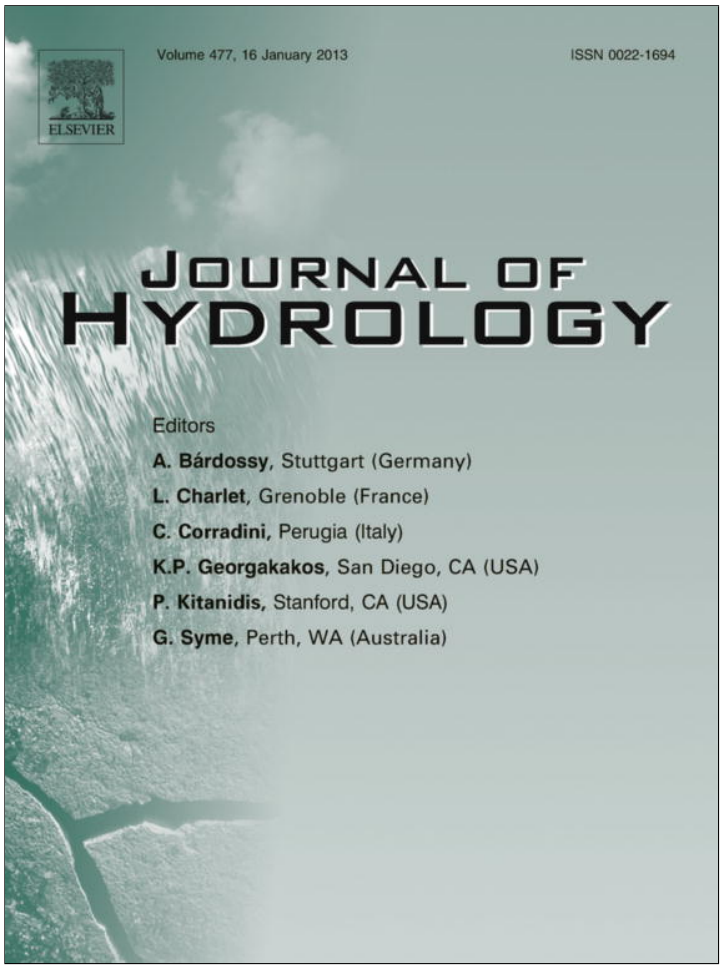

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Statistical screening for descriptive parameters for pesticide occurrence in a shallow groundwater catchment

M. Åkesson [a,*], C.J. Sparrenbom [a], C. Carlsson [b], J. Kreuger [c]

[a] Department of Geology, Lund University, Sölvegatan 12, SE-223 62 Lund, Sweden
[b] Department of Geomaterials and Modeling, Swedish Geotechnical Institute, Adelgatan 19, SE-211 22 Malmö, Sweden
[c] Department of Soil and Environment, Swedish University of Agricultural Sciences, P.O. Box 7082, SE-750 07 Uppsala, Sweden

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SUMMARY

We have assessed the ability of a range of pesticide, site and climate parameters to discriminate between detected and non-detected pesticides as observed by long-term monitoring data of pesticide use and groundwater occurrence in a small catchment in southern Sweden. Of seventeen investigated parameters, six demonstrated such an ability: dosage applied, the Henry's Law Constant (HLC), the octanol–water partitioning coefficient ($\log P_{ow}$), the amount of precipitation the week before application, the amount of precipitation the month after application, and the substance degradation potential (DT_{50}). The apparent influence of the investigated parameters on pesticide occurrence in groundwater, and their apparent suitability as descriptive parameters in terms of assessment of related risks, is accordingly discussed.

We conclude that knowledge of actual pesticide use appear fundamental for risk assessment of groundwater contamination potential. We further suggest that chemical property-parameters of specific pesticides, although clearly valuable, should be applied in groundwater contamination risk assessments with care. If site-specific values are unattainable, tabular values of log P_{ow}, HLC and water solubility (W_s) are demonstrated to exhibit a superior explanatory ability than those of substance adsorption potential (K_{oc}) and DT_{50} which, in the latter case, is shown to be able to lead to misleading conclusions on actual risks.

The demonstrated explanatory ability of precipitation both before and after application suggests that relatively greater precipitation amounts occur in relation to application of non-detected substances. Increased dilution and run-off as well as decreased soil matrix retainment and decreased top-soil cracking are potential explanations although higher-resolution monitoring records are needed in order to confirm these hypotheses.

1. Introduction

Pesticide contamination of groundwater is a worldwide concern. Residues of a large variety of compounds are found in aquifers on all inhabited continents, beneath highly variable types of environments (Gaw et al., 2008; Kolpin et al., 1998; Leistra and Boesten, 1989; Li and Zhang, 1999; Pick et al., 1992; Schipper et al., 2008; Shomar et al., 2006; Tariq et al., 2007). The problem is complex since pesticide use, although always involving a risk of unrestrained environmental spread and accumulation, is generally considered necessary in order to sustain worldwide food production (Tadeo, 2008).

During past decades, the understanding of governing parameters and processes for pesticide occurrence in groundwater has increased substantially through laboratory-studies of pesticide behaviour in different soils and sediments (e.g. Clausen et al., 2004; Sprankle et al., 1975; Tuxen et al., 2000), controlled field-scale experiments exploring the rate and pathways of transport (e.g. Boesten and van der Pas, 2000; Funari et al., 1998) and regional and national monitoring programmes comparing the degree and character of contamination between different types of catchments (e.g. Gaw et al., 2008; Steele et al., 2008; Worrall and Kolpin, 2004). Meanwhile and as a result, a range of pesticide environmental fate models (e.g. Carsel et al., 1985; Jarvis et al., 1991; Leonard et al., 1987; Tiktak et al., 2004) and pesticide environmental risk indicators (e.g. Gutsche and Rossberg, 1997; Padovani et al., 2004; Reus and Leendertse, 2000; Sorensen et al., 1998; Vaillant et al., 1995; van der Werf and Zimmer, 1998) have been developed in order to better be able to assess environmental risks associated with pesticide use. In addition to toxicological aspects, pesticide, site and climate parameters are generally considered to constitute the overall building blocks of such fate and risk analyses addressing the issue of groundwater contamination risk. However, actual data requirements may vary significantly between those different models and indicators, as may the weighting of therein applied

* Corresponding author. Tel.: +46 46 222 78 79.
E-mail address: maria.akesson@geol.lu.se (M. Åkesson).

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explanatory variables (Dubus and Surdyk, 2006; Reus et al., 2002). This shows a need for further investigation of the individual as well as relative importance of descriptive parameters of pesticide occurrence in groundwater. Not the least, there is a need for such investigations based on long-term monitoring data of pesticide occurrence in groundwater in relation to actual pesticide use (Mouvet, 2007).

1.1. Objective, motivation and hypotheses

The objective of this study is to assess the ability of a range of pesticide, site and climate parameters to discriminate between detected and non-detected pesticides in shallow groundwater beneath an intensively cultivated catchment in southern Sweden. This is done through statistical screening of a local 21-year monitoring data set of pesticide use (1990–2010) in relation to a 7-year monitoring data set of groundwater occurrence of pesticides (2004–2010). Based on the results, the apparent influence of the investigated parameters on pesticide occurrence in groundwater and their apparent suitability as descriptive parameters in terms of assessment of related risks is accordingly discussed. The aim is not to develop yet another risk assessment method, but to independently evaluate the ability of commonly used descriptive variables to explain the presence or absence of pesticides in groundwater as suggested by long-term, non-experimental monitoring data. We hereafter refer to this ability as the "explanatory ability".

The investigated parameters are: substance water solubility (W_s), substance octanol–water partitioning coefficient ($\log P_{ow}$), substance vapour pressure (V_p), substance Henry's Law Constant (HLC), substance adsorption potential (K_{oc}), substance degradation potential (DT_{50}), dosage of applied active substance, total treated area, hydraulic conductivity of treated sediments, depth to water table and distance from well from point of application, and precipitation before, after and at day of pesticide application. The choice of parameters is justified below.

K_{oc}, as measured by the affinity of a given substance to sorb to organic carbon, and DT_{50}, as measured by its soil degradation half-life, have since long been suggested to constitute a sound basis for risk assessment of pesticide contamination of groundwater (e.g. Helling et al., 1971; Hornsby, 1992). Both parameters are commonly used in related risk indicator schemes (Gustafson, 1989; Padovani et al., 2004; Reus and Leendertse, 2000), and for European Union membership states, they form the basis for environmental fate assessment and resultant decisions on authorisation through the Council Directive 91/414/EEC (European Commission, 1991). However, whereas K_{oc} and DT_{50} have been demonstrated an explanatory ability in terms of pesticide contamination of groundwater in certain studies (Gustafson, 1989; Worrall et al., 2000), Barbash and Resek (1996) stressed that this is not always the case. Potentially, K_{oc} and DT_{50} are parameters overly dependent upon surrounding environmental conditions (e.g. organic carbon and clay content of the soil) to be easily applicable as descriptive variables for risk unless site-specific values are or can be made available.

W_s, which gives an indication of the mobility of the pesticide from soil to groundwater; $\log P_{ow}$, representing the ratio of solubility of the pesticide in octanol to its solubility in water; V_p, a relative measure of the volatility of a pesticide in its pure state; and HLC, which measures a pesticide's volatility as a function of both its water solubility and its vapour pressure, are further common chemical property-parameters applied for environmental pesticide fate and risk assessment purposes (e.g. Gutsche and Rossberg, 1997; Padovani et al., 2004; Tiktak et al., 2006; Vaillant et al., 1995). Yet, observational data cast doubts on the degree of applicability of these parameters as descriptors of contamination risk. While some studies have shown a correlation between pesticide detections and compound W_s in both surface water and groundwater (Halfon et al., 1996; Kolpin et al., 1998; Kreuger and Tornqvist, 1998), Worrall and Kolpin (2004) did not manage to find such a relationship in their study of pesticide occurrence in groundwater in the mid-west United States. Furthermore, whereas Kreuger and Tornqvist (1998) found log P_{ow} to be a predictive variable for pesticide contamination of surface water, its potential as a measure of risk of groundwater contamination as suggested by observational data remains to be assessed.

Altenburger et al. (1993) and Halfon et al. (1996) both demonstrated a negative correlation between pesticide detections and compound V_p. However, both studies were conducted on surface water data and the explanatory ability in terms of groundwater contamination risk remains to be studied. HLC has been proven a determinant parameter in terms of pesticide occurrence in a surface water study by Altenburger et al. (1993). However, in a groundwater study, no such observations could be made (Kolpin et al., 1998).

The hydraulic conductivity of the treated sediments is central to many pesticide environmental risk models (e.g. Carsel et al., 1985; Jarvis et al., 1991). In terms of environmental pesticide risk indicator schemes however, this parameter as well as other site parameters such as depth to groundwater table and distance from well to point of application are less commonly adopted. They are, however common vulnerability measures in terms of overall groundwater vulnerability assessment schemes (Aller et al., 1987; Schlosser et al., 2002; Worrall and Kolpin, 2004).

Although an important part of most environmental pesticide fate models (e.g. Carsel et al., 1985; Jarvis et al., 1991; Leonard et al., 1987; Tiktak et al., 2004), the actual influence of precipitation on pesticide occurrence in groundwater, e g. its character and strength, has shown difficult to determine as it is fundamentally related to timing in relation to application (Beulke et al., 1999). This is especially true for soils and sediments exhibiting preferential flow (Gish et al., 1991; Jarvis, 2007). We have accordingly chosen to investigate the explanatory ability of a range of precipitation-parameters covering both the amount of rainfall on the specific application day, as well as the week and month before and after application.

Actual pesticide use is obviously a governing parameter in terms of potential pesticide occurrence in groundwater. However, lack of long-term monitoring data of pesticide has typically hindered real-life, i.e. field-based and non-experimental assessment and validation of actual influence. Here, we employ a unique, 21-year data set to perform such an analysis.

Our hypothesis is that all above mentioned parameters will be able to discriminate between the detected and the non-detected substances although with varying explanatory ability. This would, in turn, indicate various degrees of influence on the occurrence of pesticides in shallow groundwater, as well as various degrees of suitability in terms of use as risk assessment-parameters.

We further hypothesise that the risk of groundwater contamination is the greatest for a soluble and polar pesticide that has a low volatility and degradation potential, and that adsorbs to carbon poorly. Also, we hypothesise that the higher the applied dosage and the greater the area treated, the higher the hydraulic conductivity of the treated sediment, the thinner the unsaturated zone, the lesser the distance to well and the more the precipitation in relation to application, the greater the risk for groundwater contamination.

2. Materials and methods

2.1. Study area

The study area is located within a 9 km^2 catchment located in the southernmost part of Sweden, in one of Europe's most fertile

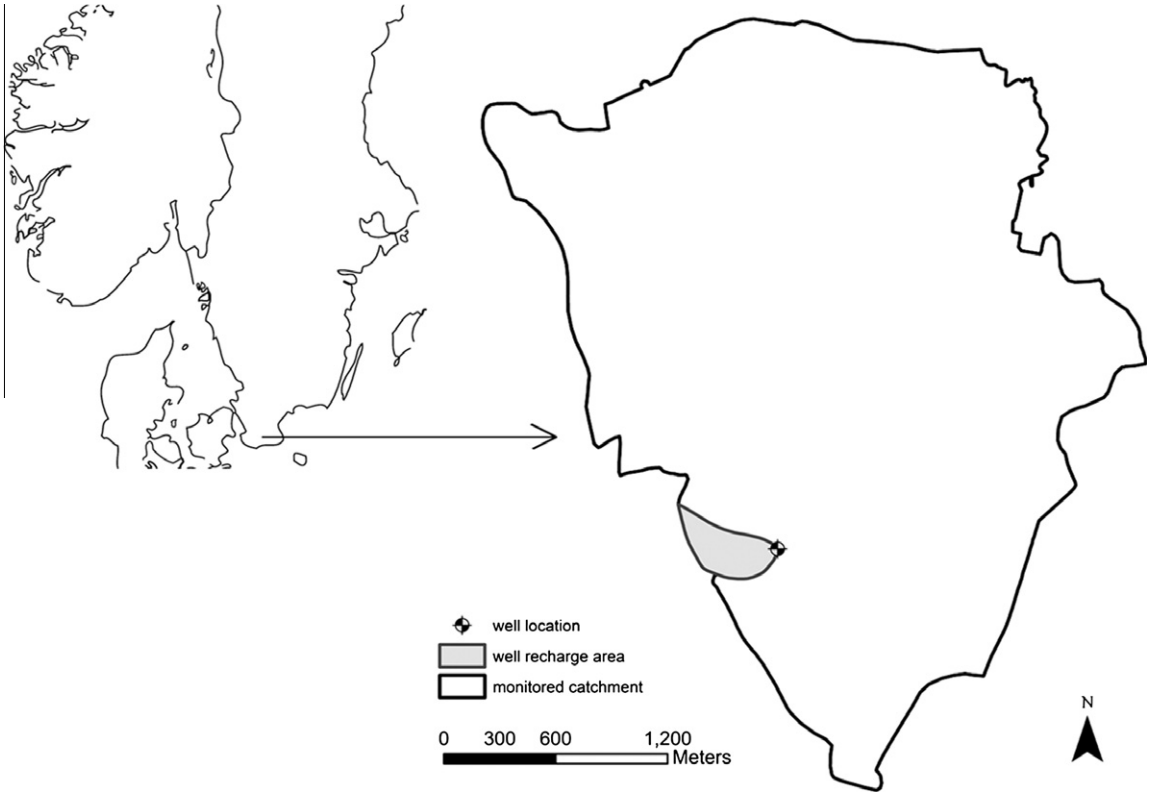

Fig. 1. Overview of study area. Right; the surface water catchment monitored for pesticide usage by the Swedish University of Agricultural Sciences, the here studied well and its estimated recharge area. *Left*: regional location.

and most intensely cultivated areas (Fig. 1). About 95% of the catchment consists of arable land, of which most is subject to a 4-year rotational cropping practice dominated by winter rape, winter wheat, sugar beet and spring barley (Kreuger, 1998). The climate is maritime with a mean annual temperature of about 7 °C and an average annual precipitation of roughly 700 mm, of which approximately 30% is available for groundwater recharge (Lewan et al., 2009). The growing season equals about 220 days.

Geologically, the region is characterised by gently undulating, glacially derived Quaternary sediments deposited within a buried Tertiary limestone bedrock valley. The thickness of the infill varies between 60 and 120 m, with a major sandy glacifluvial deposit at depth overlain by intercalating clay- and chalk-rich tills and lenses and sequences of sorted, fine-grained sediments. In the specific catchment studied, surficial sediments are dominated by a sandy loam soil consisting of 51–59% sand, 26–32% silt and 12–21% clay (Kreuger, 1998). Soil pH averages 7.2 (Svensson, 1999), surface and drainage water 7.5–8.0 (Kreuger, 1998), and shallow groundwater 7.5.

The catchment has been monitored in terms of pesticide use since 1990 through standardised documentation by the Swedish University of Agricultural Sciences in collaboration with local farmers. Since 2004, two shallow groundwater wells (filter depths: 2.9–3.5 m) located *c.* 5 m apart in the western part of the catchment have been sampled four times yearly for analysis of pesticide residues. Analyses have been adapted to known application to incorporate as many of the used substances as possible. Results from the groundwater monitoring program have been reported in annual national reports starting 2005 (Adielsson et al., 2009; Adielsson and Kreuger, 2008; Adielsson et al., 2006, 2007; Graaf et al., 2010, 2011; Tornquist et al., 2005). These reports also detail specific sampling protocols and analytical procedures.

$^{3}H/^{3}He$-analyses conducted by the Dissolved and Noble Gas Laboratory at Utah University indicate residence times of approximately 10 years for water from the so called well A, and approximately 11 years for water from the so called well B. The $^{3}H/^{3}He$-analyses were conducted according to the procedures described by Bayer et al. (1989) but in an all-metal-system yielding lower blanks. Gas model fits and resultant ages were obtained using the partial re-equilibration model (Stute et al., 1995) for well A, and the diffusive degassing model (Brennwald et al., 2005) for well B. Specific pesticide detections in well A suggest that mixing of water of residence times between at least <1 to $\geqslant$17 years occur in that well. A similar conclusion could not be drawn from the pesticide occurrence registered from well B.

2.2. Data compilation

2.2.1. Pesticide data

For retrieval of relevant pesticide data within the study area, a best-estimate recharge area of the two wells was delineated based on a groundwater surface constructed through a co-Kriging-analysis using 49 local groundwater head-measurements as a main variable, and a laser-derived national digital elevation model (©Lantmäteriet; SE < 0.5 m) as a covariate. Annual coded field maps, constructed as part of the monitoring program, were then digitalised for the recharge area permitting derivation of information on the exact timing, location and intensity of local pesticide use for the years 1990–2010.

Since analytical scope and detection limits within the groundwater monitoring program have varied over time and between substances, a correction of the data set was considered necessary in order to avoid analytical bias. Comparative studies between detected and non-detected substances can only be justified if

Table 1
Studied substances, documented detections and chemical data used in the analysis. S_w = solubility in water; log P_{ow} = octanol–water partitioning coefficient; V_p = vapour pressure; HLC = Henry's Law Constant; DT_{50} = mean soil half-life over a range of studies; K_{oc} = soil sorption coefficient.

Substance	Detected (year-month, well)	S_w (mg/L)	Log P_{ow}	V_p (mPa)	HLC (Pa m^3/mol)	DT_{50} (days)	K_{oc} (ml/g)
Aclonifen	–	1.4	4.37	0.016	3.03E−03	117	5318[b]
Bentazone	2008–02, B; 2008–04, B; 2008–08, B; 2008–11, B; 2009–02, B; 2009–08, B; 2009–11, B	570	−0.46	0.17	7.2E−05	13	55.3
Clopyralid	2006–11, A	143,000	−2.63	1.36	1.8E−11	34	5
Deltamethrin	–	0.0002	4.6	1.24E−05	3.1E−02	13	10,240,000
Dichlorprop-P	2004–11, A	590	−0.56	0.056	5.6E−05	14	44
Diflufenican	–	0.05	4.2	4.25E−03	0.0118	180	1995.5[b]
Esfenvalerate	–	0.001	6.24	1.2E−06	4.9E−04	44	5300
Ethofumesate	–	50	2.7	0.65	6.8E−04	70	166[a]
Fenpropimorph	–	4.32	4.5	3.9	2.74E−04	35	4382[a]
Fluroxypyr	2004–11, A 2007–04, A	6500	0.04	3.8E−06	1.6E−10	1	68[a]
Glyphosate	2004–11, A 2005–02, A	10,500	−3.2	0.0131	2.1E−07	12	1435
Imazalil	2009–04, A + B 2009–08, A + B	184	2.56	0.158	1.08E−04	50	3606[b]
Isoproturon	2006–11, A 2007–02, A 2007–04, A	70.2	2.5	5.5E−03	1.46E−05	12	123[a]
Lindane	–	8.52	3.69	4.34	0.15	121	1100
MCPA	2004–11, A 2006–11, A	29,390	−0.81	0.4	5.5E−05	15	31[a]
Mecoprop-P	–	860	0.02	0.23	5.7E−05	8	17[a]
Metamitron	2004–11, A	1770	0.85	7.44E−04	8.95E−08	30	77.7
Metazachlor	–	450	2.49	0.093	5.9E−05	8.6	54
Pirimicarb	–	3100	1.7	0.43	3.3E−05	86	1387[a]
Prosulfocarb	–	13.2	4.48	0.79	0.0152	31	1855[b]
Quinmerac	–	107,000	−1.41	1E−07	1E−10	30	86

All values from the FOOTPRINT PPDB database (2009).
[a] Exception: Kreuger and Tornqvist (1998).
[b] Exception: Average values from dossiers prepared by the Swedish Chemicals Agency (KEMI).

fundamental analytical boundary conditions for those substances are equivalent. Therefore, in accordance with methodology used by Kolpin et al. (1998) and Worrall et al. (2002), groundwater monitoring data was corrected to a common detection threshold of 0.01 μg/L, so that for substances with a lower specified analytical detection limit concentrations less than 0.01 μg/L were set to zero. Substances applied within the catchment and throughout the entire groundwater monitoring program detectable but never detected in concentrations $\geqslant$0.01 μg/L were accordingly defined as non-detected substances. Substances applied within the catchment and detected once or more in concentrations $\geqslant$0.01 μg/L were correspondingly defined as detected substances. Substances applied within the catchment and never detected but neither throughout the entire monitoring program detectable in concentrations $\geqslant$0.01 μg/L were excluded from further study since it cannot be ascertained that they never have occurred in concentrations at or above the defined detection threshold in one or more of the analysed samples. Whilst decreasing the sample population available for analysis, this correction ensures that only substances truly comparable in terms fundamental analytical boundary conditions are included in the analysis.

For well B, the data set correction meant too heavy a reduction of data for sound quantitative statistical investigation. For well A, the correction constrained the data set to 19 of 58 substances applied in the recharge area since 1990 (Table 1). Two additional substances for which there are no records of use met the above analytical criteria and were accordingly incorporated into the study. One of these is the seed treatment substance imazalil, which has probably been used in the area along with sowing at multiple occasions without documentation. The other is lindane, which was phased out during the 1980s in Sweden suggesting either non-documented or pre-1990-application.

For the 21 substances, dosage and total area treated per application was calculated. Typical tabular values of chemical properties (W_s, log P_{ow}, V_p, HLC, DT_{50} and K_{oc}) were collected from the comprehensive, relational FOOTPRINT Pesticide Properties Database (PPDB, 2009). Values which could not be attained from the PPDB were collected from Kreuger and Tornqvist (1998) and the Swedish Chemicals Agency (KEMI, 2012). Using tabular values from a widely available relational database is a conscious choice made by the authors; partly due to economical restrictions impeding determination of site-specific values, mainly however, in order to study the explanatory ability of readily accessible data as it is commonly this type of data that is used for general risk assessment purposes (e.g. Guerbet and Jouany, 2002; Padovani et al., 2004).

2.2.2. Site data

The hydraulic conductivity of the sediments within the study area was estimated based on a digital version of the Swedish Geological Survey's Quaternary deposits map (scale 1:50,000, mapping-depth: 50 cm). Three areas of varying sedimentary character were recognised: clayey till, silty-sandy till and postglacial sand. The areas were digitalised using ArcGIS, and given a hydraulic conductivity-index of 0, 1 and 2 respectively. The indexing acknowledges the theoretical concept of increasing conductivity (and permeability) with increasing average grain-size and increasing degree of sorting (Fetter, 2001). However, it does not consider the potential for preferential flow which can be significant in clayey till deposits (Jarvis et al., 2007). Calculations of an average conductivity-index for each application were conducted through automated spatial analyses of the digitalised field and sedimentary maps in ArcGIS.

The average distance from site of application to well was calculated for all applications using ArcGIS and the digitalised field

Table 2
Results of statistical analyses for investigated parameters (two significant figures). Bootstrapped confidence intervals (CI) were compared at significance-level-intervals of 0.05 down to the 0.4-level. If two or more analyses of a specific parameter demonstrate a significant difference at a level of ⩽0.1 between the two groups, the parameter is considered to be statistically significant in terms of risk for pesticide contamination of groundwater. Applied dosage of active substance, amount of precipitation week before and month after application, logP_{ow}, HLC and soil DT_{50} are accordingly indicated to constitute explanatory ability for risk of pesticide contamination of groundwater in the studied catchment.

Parameter	Group 0		Group 1		*t*-Test for equality of means (*p*)	Independent-samples median test (*p*)	Bootstrapped level of significance; means (*p*) [CI group 0];[CI group 1]	Bootstrapped level of significance; medians (*p*) [CI group 0]; [CI group 1]
	Mean	Median	Mean	Median				
Dosage (g/ha) per app.	200	100	600	600	<0.0001	<0.0001	0.01 [160–250]; [520–670]	0.01 [94–130]; [400–700]
Tot. area (ha) treated per app.	1.1	0.47	1.3	0.68	0.24	0.019	>0.4	>0.4
Hydraulic conductivity-index per app.	1.0	1.0	1.0	1.0	0.37	0.53	>0.4	>0.4
Av. distance (m) from well per app.	250	250	230	250	0.34	0.51	>0.4	>0.4
Av. distance (m) to gw-surface per app.	2.9	3.0	3.0	3.0	0.13	0.86	0.4 [2.9–2.9]; [3.0–3.0]	>0.4
Rain (mm) per day of app.	1.5	0	0.92	0	0.25	0.96	>0.4	>0.4
Rain (mm) week before app.	10	6.5	8.9	3.5	0.20	0.006	>0.4	0.1 [5.3–8.5]; [2.9–4.8]
Rain (mm) week after app.	12	6.6	10	5.5	0.38	0.34	>0.4	>0.4
Rain (mm) month before app.	45	37	44	38	0.75	0.83	>0.4	>0.4
Rain (mm) month after app.	56	49	49	42	0.017	0.13	0.1 [52–59]; [45–51]	0.25 [46–52]; [39–46]
Rain-lag (days) if 0 rain on day of app.	3.9	2.0	3.9	2.0	0.98	0.72	>0.4	>0.4
W_s (mg/L)	8600	13	2.4E4	4100	0.38	0.08	>0.4	0.2 [4.3–450]; [590–18,000]
LogP_{ow}	2.9	3.7	−0.16	−0.26	0.007	0.18	0.05 [1.7–4.0]; [−1.5–1.2]	0.1 [1.7–4.5]; [−1.7–1.7]
V_p (mPa)	0.82	0.17	0.25	0.035	0.31	0.66	0.3 [0.43–1.2]; [0.12–0.41]	>0.4
HLC (Pa m^3/mol)	0.016	4.9E−4	2.9E−5	7.4E−6	0.28	0.024	0.01 [4.6E−4–0.048]; [1.9E−6–7.0E−5]	0.01 [3.3E−5–0.015]; [8.9E−11–8.2E−5]
Soil DT_{50}	58	35	21	15	0.073	0.18	0.1 [37–83]; [13–30]	0.40 [31–44]; [13–23]
K_{oc}	7.9E5	1400	760	73	0.45	0.18	0.25 [1500–1.6E6]; [240–1400]	0.35 [190–2000]; [76–160]

maps. The laser-derived national digital elevation model and the interpolated groundwater surface were used to calculate average depth to groundwater table at site of application.

2.2.3. Climate data

Precipitation data was collected from a weather station located *c.* 2 km NE of the wells. For all applications, calculations were made for amount of precipitation per application day, per week before and after application and per month before and after application. Further, a rain-lag index defined as amount of days until rainfall after application was calculated based on the assumption that if no rain falls on the day of application, the time-lag until rain will be negatively correlated to the risk for groundwater contamination. That is, the longer the time until rainfall, the lesser the risk for contamination.

2.3. Statistical analysis

In accordance with the general methodology outlined in the objective-section, compiled pesticide, site and climate data were sorted into two groups; group 0 containing all data concerning the non-detected substances, and group 1 containing all data concerning the detected substances. Data on pesticide use, site and climate conditions relating to applications of detected substances occurring *after* the last detection of the respective substances were discarded. I.e., for a given detection of a specific substance, only the applications of that substance occurring *before* that detection can have resulted in the detection. Pesticide, site and climate data relating to a total of 211 applications for the seven substances in group 1 could accordingly be compared to those of 233 applications for the twelve substances in group 0.

Group-wise means and medians were calculated for all investigated parameters, i.e. dosage per application, total treated area per application, average hydraulic conductivity per application, average distance from well per application, average depth to water table per application, amount of precipitation at day of application, amount of precipitation during the week and month before and after application, rain-lag (if 0 precipitation on day of application), W_s, log P_{ow}, V_p, HLC, DT_{50} and K_{oc}. The means for the two groups were then compared, parameter by parameter, using the independent samples *t*-test to test the null hypothesis that the means were equal. Further, group-wise medians were compared, and the null hypothesis that the medians were equal was tested using the independent-samples median test.

Next, confidence intervals for the respective data set means and medians were estimated and compared through bootstrapping (Efron, 1979), again parameter by parameter and group-wise. The bootstrap process was conducted in MATLAB R2010b and involved 1000 repetitions of random resampling with replacement of the original data sets. The resulting 1000 means and medians for each data set were used to better understand and constrain the distribution of the various sample populations, providing a more robust basis for comparison than only the basic sample summary statistics independently.

All results were analysed jointly, and when two or more analyses indicated a statistically significant difference between groups for a certain parameter at a level of $\leqslant 0.1$, the difference and hence the explanatory ability of that parameter was considered to be statistically validated.

3. Results

Table 2 lists the results of all statistical analyses.

3.1. Pesticide parameters

All statistical analyses demonstrate a significant difference in applied dosage between the non-detected and the detected substances. The detected substances are generally applied in higher dosages ($\bar{x} = 600$ g/ha,$M = 600$ g/ha) than the non-detected substances ($\bar{x} = 200$ g/ha,$M = 100$ g/ha). None of the other investigated parameters show a similar magnitude of difference.

For total area treated, the analyses demonstrate a tendency for the detected substances to have been applied over larger areas ($\bar{x} = 1.3$ ha/app,$M = 0.68$ ha/app) than the non-detected substances ($\bar{x} = 1.1$ ha/app,$M = 0.47$ ha/app). However, the difference is too small to yield any statistical significance with the exception of the independent-samples median test.

Three of the chemical parameters studied, $\log P_{ow}$, HLC and DT_{50}, demonstrate statistically significant differences in property values between the two groups. Overall, the non-detected substances exhibit larger values for all three properties than the detected substances. This suggests that the detected substances are more polar, less volatile and more degradable in soil than non-detected substances.

None of the other chemical parameters tested (W_s,V_p,K_{oc}) show significant differences between groups.

3.2. Site parameters

None of the investigated site parameters, i.e. hydraulic conductivity, depth to water table and distance from well to point of application, demonstrate any statistically significant difference between groups. Yielded sample populations are virtually identical.

3.3. Climate parameters

The statistical analyses of precipitation amounts in relation to pesticide application demonstrate a statistically significant difference between groups with regard to the amount of rain falling the week before application and the amount of rain falling the month after application. The amount of precipitation the week before application of detected substances is overall less ($\bar{x} = 8.9$ mm,$M = 3.5$ mm) than the amount of precipitation the week before application of non-detected substances ($\bar{x} = 10$ mm,$M = 6.5$ mm). Likewise, the amount of precipitation the month after application of detected substances is overall less ($\bar{x} = 49$ mm,$M = 42$ mm) than the amount of precipitation the month after application of non-detected substances ($\bar{x} = 56$ mm,$M = 49$ mm).

None of the other precipitation variables show any statistically significant differences between groups.

4. Discussion

4.1. Quality of the monitoring data set

The key data set forming the basis of this study is that of pesticide use as documented and reported by the local farmers to the Swedish University of Agricultural Sciences 1990–2010. This data set is inevitably subject to uncertainties as the documentation relies on the honesty of the farmers, and their willingness to collaborate. Overall the data is considered of high quality and probably unique in its kind. With one exception, all farmers within the catchment have been part of the research programme since its start, continuously documenting their pesticide use according to standardised protocols. Even illegal use of banned substances has been reported, and the same data set has further proven valuable for studies of pesticide contamination of surface water (Kreuger, 1998; Kreuger et al., 1999; Kreuger and Tornqvist, 1998).

Of greater concern is the groundwater monitoring data with regard to quantity. Even though samples are being and have been taken four times yearly, the amount of data generated is relatively limited. More frequent sampling would allow for a higher resolution-record which would constitute a better basis for analysis as the sample population would increase. However, in this respect, the methodological approach taken is considered robust as it takes into consideration four statistical analyses per investigated parameter; two of which explores and compares the distribution of the sample populations.

4.2. Results vs. hypotheses: explanatory ability and apparent influence of the investigated parameters

Of the seventeen parameters investigated, only six were able to discriminate between the detected and the non-detected substances; dosage, HLC, log P_{ow}, amount of rain the week before application, amount of rain the month after application, and DT_{50} (ranked according to explanatory ability). For the remaining eleven parameters; total treated area, average soil hydraulic conductivity and distance from well, average depth to water table, amount of precipitation at day of application, amount of precipitation the week after and the month before application, rain-lag, W_s, V_p and K_{oc}, differences between the two groups were too small to yield statistical significance. That is, they exhibited no satisfactory explanatory ability in terms of pesticide contamination of groundwater within the studied catchment.

4.2.1. Pesticide parameters

As hypothesised, the results suggest that the risk of groundwater contamination is fundamentally dependent upon dosage; the larger the amount of a specific pesticide applied over a certain area, the higher the risk. Whilst expected, as to our understanding, no previous studies have been able to so directly demonstrate this based on detailed long-term, non-experimental data of actual use (as opposed to estimations on use based on land-use or pesticide sales (e.g. Bartos et al., 2009; Kolpin et al., 1998)). It is clear that in order to assess the risk of groundwater contamination of pesticides, knowledge of actual pesticide loading is essential. Dosage alone exhibits the greatest explanatory ability of all studied parameters.

The size of the treated area alone is clearly not as good a discriminator. Although the results do show the expected tendency of detected substances to have been applied over relatively larger areas than the non-detected substances, the difference is not statistically significant. As the comparison is made based on 21 years of monitoring data of pesticide use within a single and relatively small rotational-cropping catchment that has roughly exhibited the same field-configuration throughout, spatial differences are likely averaged out over time. There is likely more potential for using total treated area as a descriptive variable for assessment of relative risk of pesticide contamination between or within catchments that exhibit widely varying land-use, as it would introduce more pronounced spatial disparity (e.g. Barbash and Resek, 1996; Sorensen et al., 1998).

The screening for chemical property-parameters indicates that HLC, log P_{ow} and DT_{50} independently all exhibit an explanatory ability in terms of pesticide contamination of groundwater. As for HLC and log P_{ow}, results confirm the original hypothesis suggesting that the less volatile and the more polar a substance, the more likely it is to contaminate groundwater. The findings of Altenburger et al. (1993) and Kreuger and Tornqvist (1998) of correlations between surface water pesticide detections and HLC and log P_{ow} respectively are hence suggested to apply also for groundwater environments. Accordingly, HLC and log P_{ow} appear as suitable chemical-property parameters for risk assessment of pesticide contamination of groundwater.

However, for DT_{50}, results indicate that detected substances would be more easily degradable than non-detected substances. This opposes the original hypothesis. There are, however, potential explanations for this outcome. Firstly, it could be a result of using tabular instead of site-specific values. If so, this indicates the necessity of the latter, and the inappropriateness of the former with regard to the applicability of DT_{50} as a descriptive variable for risk assessment of pesticide contamination of groundwater. Secondly, the outcome could be an indication of the presence of preferential flows, which would serve to increase the transport and contamination potential of otherwise rapidly degrading substances (Elliott et al., 2000; Jarvis, 2007). Theoretically, however, this would only serve to minimise the differences in contamination potential of substances with varying degrading potential and not to increase the risk of contamination of otherwise easily degradable substances. Thirdly, as suggested in a study by Kreuger and Tornqvist (1998), it could also be that the overall poorer ability of the detected substances to sorb to soil compensates their overall greater degradability. The fact that the detected substances overall exhibit a greater degradation-potential than the non-detected substances could potentially be explained by the fact that the detected substances overall exhibit a relatively poorer ability to sorb to soil which infers a relatively greater potential for leaching. This would then mean that K_{oc} is a more important parameter in terms of pesticide contamination risk of groundwater than DT_{50}. However, it should then be noted that the difference between the detected and the non-detected substances in terms of sorption coefficients is not statistically significant.

Why then, are neither W_s, V_p nor K_{oc}, able to discriminate between the detected and non-detected substances in this study? All three are chemical property-parameters commonly used for environmental pesticide risk assessment-purposes (e.g. Carsel et al., 1985; Guerbet and Jouany, 2002; Gutsche and Rossberg, 1997) and have, as noted, shown to exhibit a descriptive ability in terms of pesticide contamination of surface (V_p: Altenburger et al., 1993; Halfon et al., 1996) and groundwater (W_s, K_{oc}: e.g. Kolpin et al., 1998). Inevitably, using tabular values instead of site-specific values is an issue relevant also here and could be a reason for the lack of explanatory ability. Further, it is clear that the analyses conducted with regard to the chemical property-parameters are sensitive to extreme values due to the relatively low sample population. For example, quinmerac, which sorts under the non-detected substances, has an extremely high solubility value that disproportionately affects the summary statistics of its group. Upon removal of quinmerac from the analysis, the difference in W_s between the detected and non-detected substances becomes statistically significant thus supporting the findings of earlier studies (Kolpin et al., 1998). Quinmerac is by far the least used pesticide in the data set, i.e. it is only applied twice in the area throughout the entire monitoring program hence this might be considered a valid exclusion. It should also be noted that HLC – a combination of W_s and V_p – does exhibit an explanatory ability thereby indicating a certain degree of *joint* explanatory ability of W_s and V_p. In order for V_p to matter in terms of groundwater contamination potential, possibly, much greater values than those exhibited by the substances studied here are needed.

Lastly, preferential flow minimising differences in contamination potential of substances with varying chemical properties, could be the reason for the lack of explanatory ability of W_s, V_p or K_{oc} as was discussed in relation to DT_{50}.

4.2.2. Site parameters

For the investigated site parameters, group-wise means and medians are, as noted, virtually identical which suggest a lack of explanatory ability for those parameters. However, this does not necessarily imply that they are unsuitable as descriptive variables for estimation of risk of groundwater contamination. First, since the site parameters studied are dependent upon field-configuration, the concerns raised regarding the treated area-parameter are also relevant here. I.e., spatial differences can be expected to average out over time when the comparisons are made based on monitoring data from a single and relatively small rotational-cropping catchment that roughly exhibits the same field-configuration throughout the studied time period. The hydraulic conductivity of the treated sediments, the distance to well and to the groundwater surface from the point of application may likely constitute suitable descriptive variables in terms of relative risk assessment of groundwater contamination with regard to comparisons between catchments of varying physical and land-use properties, or between single pesticide applications (e.g. Barbash and Resek, 1996; Schlosser et al., 2002; Tiktak et al., 2004). However, this is likely not the case when attempting relative environmental risk assessment for the use of specific pesticides within relatively small areas dominated by rotational cropping practices such as the catchment studied. Consideration needs then (and overall) be given the long-term perspective.

Furthermore, it is plausible that at least part of the inability of the studied site parameters to discriminate between the detected and the non-detected substances could relate to the presence of fractures and preferential flow within the more clayey parts of the catchment. This would lessen the hypothesised differences in hydraulic conductivity with average grain-size within the catchment (Nilsson et al., 2001) and therefore also decrease the importance of distance to well and groundwater surface from application. Based on detailed investigations of modes of pesticide transport to groundwater in similar Danish environments (Jorgensen et al., 2002), this appears very reasonable. The marked difference in detected substances between close-lying well A and well B (Table 1), as well as the indicated mixing of water of residence times between at least <1 to $\geqslant$17 years in the studied well A, further corroborates the hypothesis that preferential flow constitutes an important pathway for pesticide transport to groundwater in the studied catchment.

4.2.3. Climate parameters

Of the precipitation-parameters studied, it is only the amount of rain falling the week before application and the amount of rain falling the month after application that demonstrated an ability to discriminate between the detected and the non-detected substances, indicating that the detected substances experience significantly less precipitation both before and after application than the non-detected substances. Although none of the other precipitation indices show any overall statistically significant differences between groups, the tendency for relatively less precipitation to occur both before and after the application of the detected substances is present throughout with the exception of the rain-lag index and the median amount of precipitation the month before application for which differences are minor. The outcome is against the original hypothesis assuming that relatively high amounts of rainfall before and after application should favour pesticide transport to

groundwater as potential recharge rates would increase. Why is the exact opposite relationship suggested here?

Firstly, it should be noted that in absolute terms, the statistically significant differences in precipitation amounts between the two groups of substances are only a few millimetres and perhaps an insufficient amount to matter in terms of actual transport potential. Also, sources of errors regarding the precipitation data exist since e.g. wind-loss and evapotranspiration has not been accounted for. Local measurements thereof do not exist. As a test, analyses were however carried out accounting for regional evapotranspiration-losses as suggested by back-modelled data from the regional hydrological HYPE-model (Lindström et al., 2010). The results smooth out group-wise differences throughout and no statistical significance remain. Since the evapotranspiration data is modelled over a 23 km^2 area with generalised input data, it however inherently also suffers from sources of error. This is demonstrated in Lindström et al. (2010), where the HYPE-modelled evapotranspiration managed to explain slightly more than half of measured evaporation at a specified test-site. Accordingly, it is not necessarily the case that the precipitation data adjusted for evapotranspiration is more correct than the unadjusted data. Hence, we think it is viable to discuss potential inferences of the statistically significant differences as indicated by the only site-measured data available. The concerns ought, however, to be acknowledged, and the inferences made should be considered with caution.

A simple yet plausible explanation for the indicated tendencies of the non-detected substances to overall experience relatively greater precipitation amounts is that the greater precipitation amounts serve to dilute the applied pesticide amounts and thereby also lessen potential groundwater concentrations. Whilst potentially explaining the presence or absence of pesticides as recorded in groundwater samples it is worth emphasising that dilution would not, however, serve to infer a lesser or greater groundwater contamination risk per se, only resulting concentrations. Whether or not the absolute difference in amounts of precipitation between the two groups is big enough to cause major differences in terms of these two processes is questionable. A higher-resolution pesticide monitoring record would be needed in order to resolve this, i.e. in order to study transport and resultant groundwater concentrations in relation to singe applications.

Other studies who have reported relatively less pesticide transport from wet than from dry soils have further suggested increased soil matrix incorporation and retainment in relatively wetter soils (Shipitalo et al., 1990), and increased top-soil cracking allowing for increased downward flow of water and associated solutes during relatively drier periods of time (Brown et al., 1995) as plausible explanations. It could also be the case that increased run-off in relation to greater precipitation amounts could result in decreased groundwater contamination potential.

4.3. Overall implications and issues

As stated in the introduction, the aim of this study was to evaluate the individual and relative ability of a range of pesticide, site and climate parameters commonly used as descriptive variables in existing pesticide environmental risk assessment schemes, to explain the presence or absence of pesticides in groundwater as suggested by long-term, non-experimental monitoring data (corrected for variable analytical boundary conditions). Although the data set has the potential for validation of specific risk models and indicators, we opted for an independent evaluation with a relatively broad approach aimed at providing an "observational data fundament" for prospective discussions on strengths and weaknesses of a number of existing models and indicators (e.g. SYNOPS: Gutsche and Rossberg, 1997; MACRO: Jarvis et al., 1991; EPRIP: Padovani et al., 2004; FOOT-CRS: Reichenberger et al., 2008; EYP: Reus and Leendertse, 2000; HD: Sorensen et al., 1998; SIRIS:Vaillant et al., 1995). Covering all variables and aspects of these models and indicators is beyond the scope of this study, as is therefore also judgments on their overall set-up and potential performance. Yet, some general inferences can be made.

Overall, it seems appropriate to suggest that applied pesticide dosage has the greatest explanatory potential in terms of pesticide presence or absence in groundwater. As such, with regard to related risk assessment, knowledge of pesticide loading is fundamental and ought to be treated as a key variable as is the case for most existing risk models and indicators (e.g. Gutsche and Rossberg, 1997; Padovani et al., 2004; Reus and Leendertse, 2000; Sorensen et al., 1998; Vaillant et al., 1995; van der Werf and Zimmer, 1998).

Chemical property-parameters of specific pesticides further undoubtedly exhibit explanatory ability in terms of pesticide contamination of groundwater. However this study highlights some important issues concerning their applicability for related risk assessment. As demonstrated, the use of tabular values always introduces analytical uncertainty potentially leading to misleading conclusions as discussed in relation to analysis outcomes regarding DT_{50}. If possible, site-specific values should therefore be used. In the absence of such values, which is often the case due to economical restrictions, this study indicates that tabular values of relatively less site-dependent parameters such as log P_{ow}, HLC and likely also W_s exhibit a relatively greater explanatory ability and as such are preferable for risk assessment. Similar inferences have been the starting-point of other studies taking things further and demonstrating, based on observations of pesticide occurrence or absence in groundwater, that there is even scope for applying empirical molecular descriptors obtainable without measurement error or site-specific variability as descriptive variables in related risk assessment models and indicators (e.g. Worrall and Kolpin, 2004; Worrall and Thomsen, 2004).

Further, V_p as an independent measure of groundwater contamination risk cannot be supported by this study. However, its joint influence together with W_s is demonstrated through the explanatory ability of HLC. This highlights the importance of estimating and appropriately addressing not only the independent but also the joint influence of chemical property-parameters. Especially, as discussed in relation to K_{oc} and $DT_{50,}$ since one property may affect the potential influence and hence explanatory ability of another.

Another point to be made is the importance of risk assessment of pesticide contamination of groundwater to be able to account for the occurrence of preferential flow. This is hardly news to the modelling-community (Dubus and Surdyk, 2006; Jarvis et al., 1991; Vanclooster et al., 2000). In terms of environmental pesticide risk indicator-schemes however, this appears to be a seldom considered parameter. If preferential flow is a plausible means of pesticide transport to the subsurface, then dominant mechanisms of overall transport of pesticides to groundwater may alter together with the explanatory ability of otherwise descriptive variables. Not accounting for preferential flow when this is a plausible means of transport into the groundwater environment may therefore deteriorate risk assessments made.

Precipitation is clearly an important variable to consider in terms of risk assessment of pesticide contamination of groundwater. However, it is evident that a simple, general conclusion on the strength and character of its influence is proving difficult to constrain as it may alter according to prevailing site conditions and local pesticide use patterns. Obviously, precipitation is necessary for infiltration, groundwater recharge and contamination to occur. Hence, on a large regional or national scale, relative precipitation amounts as a positively correlated measure of groundwater contamination risk might be valid (e.g. Tiktak et al., 2004). However,

on a more detailed note, it might be that dilution and run-off in relation to relatively larger amounts of precipitation, enhanced soil matrix incorporation and retainment in relatively wetter soils (Shipitalo et al., 1990), as well as increased top-soil cracking allowing for increased downward transport of water and associated solutes during relatively drier periods of time (Brown et al., 1995) need to be considered in terms of contamination potential.

5. Conclusions

The overall findings of this study demonstrate an ability of pesticide use and -chemistry parameters, as well as precipitation parameters, to discriminate between detected and non-detected substances as suggested by long-term, non-experimental monitoring data corrected for variable analytical boundary conditions. Spatially-dependent parameters such as total treated area, hydraulic conductivity of the treated sediments and distance to groundwater surface and well to point of application did not exhibit a similar ability. This might, however, be a result of spatial differences averaging out over time when the presence and absence data is a result of multiple applications from within a rotational-cropping catchment that has roughly exhibited the same field-configuration throughout the studied time interval. Specific conclusions are as follows:

- Of the studied parameters, applied dosage exhibits the overall greatest explanatory ability in terms of pesticide presence or absence in groundwater. Knowledge thereof consequently appears fundamental for related risk assessment and should be treated as a key parameter.
- Whilst valuable, chemical property-parameters of specific pesticides should be applied in groundwater contamination risk assessments with care. If site-specific values are unattainable, tabular values of log P_{ow}, HLC and W_s appear to exhibit a greater explanatory ability than those of K_{oc} and DT_{50}. Potential effects of one chemical property-parameter on the explanatory ability another further need to be considered.
- Whilst a prerequisite for estimation of overall contamination potential, in more detail, relatively more precipitation both before and after pesticide application may serve to decrease resultant groundwater concentrations and thus likelihood for detection. Dilution, increased run-off, decreased soil matrix retainment (Shipitalo et al., 1990) and decreased top-soil cracking (Brown et al., 1995) are potential explanations. More and higher-resolution studies of the effects of precipitation on pesticide contamination potential of groundwater in different environments and in relation to actual pesticide use are needed in order to be able to better and more accurately account for the resultant effects in terms of risk assessment of pesticide contamination of groundwater on different scales.
- If preferential flow is a plausible means of transport of pesticides into the groundwater environment, this is a parameter that needs to be considered for risk assessment purposes as it may alter the strength and character of the explanatory ability of otherwise descriptive variables.

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