Pesticides in Groundwater: Some Observations on Temporal and Spatial Trends

D.J. Lapworth, MRes, AMRSC, Geochemist [1*]
D.C. Gooddy, PhD, Csci, CChem, MRSC, FGS, Senior Geochemist [1]
M.E. Stuart, BSc, CChem, MRSC, Senior Hydrogeochemist [1]
P.J. Chilton, MSc, CGeol, FGS, Principal Hydrogeologist [1]
G. Cachandt, MSc, FGS, Asset Manager [2]
M. Knapp, PhD, Regulatory Scientist [2]
S. Bishop, MSc, Water Quality Scientist [2]

[1]British Geological Survey, Maclean Building, Wallingford, Oxon, OX10 8BB, UK
[2]Yorkshire Water Services Ltd, Western House, Halifax Road, Bradford, BD6 2LZ

[*]Corresponding author. Tel +44-01491-692327

E-mail address: djla@bgs.ac.uk (D.J. Lapworth)

ABSTRACT

Following a monitoring programme of private shallow boreholes a total of 22 different pesticides were detected in 14 shallow boreholes in the Triassic Sherwood Sandstone aquifer of South Yorkshire between January 2002 and November 2003. Of the 294 positive detections made, 34% were detected in excess of the prescribed concentration or value (PCV) (drinking water standard) for individual pesticides. Pesticides were detected in 11 (78%) of the boreholes, and in 8 (57%) at concentrations exceeding the PCV on at least one occasion. These findings were complemented by data from deeper boreholes in which concentrations exceeding the PCV were also detected. Pesticide occurrence could be related to landuse; mecoprop and isoproturon were frequently detected at several locations reflecting the arable landuse, dicamba at a golf course, and atrazine, propazine and terbutryn near a railway. Temporal variations have emerged at individual sites and across the study area as the result of extended and frequent monitoring.

Keywords: pollution, groundwater, pesticides, mecoprop, isoproturon, landuse, Sherwood Sandstone

INTRODUCTION

Several recent studies have described the transport of pesticides from the soil to depth within different groundwater systems (1-3) as well as the occurrence of their metabolites (4,5). Reducing the impact of anthropogenic pollution on UK aquifers and ameliorating any deterioration of water quality is central to key legislative drivers such as the EU Water Framework Directive (WFD) (6) and the proposed Daughter Directive relating to the protection of groundwater (7). This is also central to specific measures in the UK relating to pesticides such as the Voluntary Initiative scheme (8). The Drinking Water Regulations (9) that transpose the EC Drinking Water Directive (10) into UK law set an exceedingly low standard Prescribed Concentration or Value (PCV) for individual pesticides in water supplied to customers of 0.1 µg/l.

Some pesticide sources are closely related to present or historical landuse and therefore may help in understanding the spatial occurrence of pesticides within an aquifer. Potential sources related to landuse include arable agriculture (3), transport networks (11), golf courses (12) and landfills (13). Table 1 shows some examples of pesticides that may be associated with different landuses. A major pathway for contaminant transport to groundwater is leaching from soils following pesticide application. Drains, soakaways, sumps and fractures can provide rapid transport routes to groundwater which by-pass some of the natural attenuation potential provided by the soil and shallow unsaturated zone.

Pesticide occurrence in groundwater has also been found to be dependent on the persistence and mobility of the different compounds in the aquifer (14). The persistence and mobility vary due to intrinsic properties of the individual compounds. The Groundwater Ubiquity Score or GUS index, based on the K_{oc}, the affinity with organic carbon and a measure of mobility, and the half-life of compounds as a measure of persistence, can be used as an indication of the potential for pesticide leaching to the groundwater (15). Molecular properties, connectivity/structure, of pesticide compounds have also been used in recent studies to understand and predict the occurrence of pesticides in groundwater (16).

Assessing the extent of pesticide contamination within aquifer systems and understanding the transport of pesticides to groundwater from diffuse and point sources is of major importance for management of groundwater resources. This is critical in aquifers such as the Triassic sandstone of South Yorkshire which currently accounts for the entire public water supply water in the Doncaster region, and 6% of Yorkshire Waters overall supply.

Associated with the wet autumn and winter of 2000-2001, water levels and concentrations of nitrate in abstracted groundwater increased rapidly in many parts of the country. Against this national background, Yorkshire Water PLC also observed a possible increase in trace pesticide concentrations in water drawn from the sandstone aquifer for supply in the Doncaster area. Affected sources are currently blended with other sources before going into supply.

A groundwater survey of shallow (for the purpose of this study taken as <30 mbgl) private boreholes in the Doncaster area was carried out between January 2002 and November 2003, augmented by data from deeper boreholes within the sandstone aquifer between March 2000 and January 2004. This paper builds on some of the initial work of Gooddy et al (17). It makes some observations on the spatial and temporal variations in pesticide concentrations and the relationship between pesticides detected in groundwaters and landuse within the catchments of public supply abstraction boreholes in the Doncaster area. This will provide better understanding with regard to future trends in pesticide occurrence and will support the decision making process regarding the long-term water resource management strategy for the area.

BACKGROUND: DESCRIPTION OF STUDY AREA

Landuse, Pathways and Sources of Pesticides

Figure 1 shows the sampling locations in relation to land-use within the Doncaster study area. The landuse data are taken from the digital Land Cover Map of Great Britain (2000) (18). The landuse is predominantly arable, largely a potential diffuse source of pesticides although soakaways are a possible point source from washings of tanks and disposal of residual compounds. Arable landuse includes cultivation of cereals, and root crops: beet, carrots and potatoes. Other landuses include semi-natural woodland, moor and grassland, used for grazing and silage, as well as areas of urban development. The semi-natural cover is discontinuous, with moorland dominating in the east of the area. Urban areas are largely to the west, including Doncaster and its surrounding villages, as well as Hatfield to the north and Finningley to the south. A single motorway runs east to the south of Doncaster and cuts northwards through the centre of the study area. Two railway lines are located to the south and one to the north of the area. There is a golf course in the west of the study area and another is sited in the south.

The local authority, pre-Environment Agency, had a range of categories for landfill gas emissions based on waste type received by the landfill. The category was on a sliding scale, a class 1 landfill being the highest risk class for gas emissions, and indicates hazardous waste, and a class 4 landfill indicates probable inert waste only. The study area has twenty-five landfills in all, eight are class two, one is class three, and sixteen are class four. Two class two landfill sites, which are potential point sources, are in relatively close proximity to four sample sites, S3, S5, S11 and S14 are shown in Figure 1.

Estimates of agricultural pesticide applications were obtained for Parish Groups in the study area from Produce Studies, which forms part of Promar International, Newbury. Data on pesticide usage on arable land in the Doncaster and Selby area between 1994 and 2001 is shown in Figure 2. There has been an overall reduction in the total amount of key pesticides applied; mecoprop, isoproturon, bentazone, atrazine and simazine, during this period. Mecoprop has been gradually replaced with the more biologically active mecoprop-p (MCPP), with these applications occurring in the early summer between March and May. Detailed records of pesticide usage were only available for three survey sites. At these locations applications were also concentrated in the summer months, with limited applications in the winter for winter wheat.

Drift Cover and Aquifer Vulnerability

The cover of Quaternary deposits in the study area is very complex and contains a wide range of lithologies with differing hydraulic conductivities (19). Some of these provide hydraulic connectivity with the sandstone aquifer and others act as an aquitard. The aquifer vulnerability classifications for the study area are shown in Figure 3. The major aquifer vulnerability classifications for the study area (20) are high and intermediate for the most part, with low-permeability quaternary deposits only present north of the study area providing a degree of protection to the aquifer. The thickness of the unsaturated zone is variable and relatively thin, 7-17m, resulting in short travel times within the unsaturated zone. The variation in unsaturated zone thickness is largely due to the effects of local abstraction, as the topography is very subdued across the study area.

Groundwater Movement

The bedrock geology of the area comprises Permian and Triassic rocks which dip at 1-2° to the east and lie unconformably on Carboniferous Coal Measures. The Triassic Sherwood Sandstone overlies a mixed sequence of Permian mudstones, marls and siltstones. The Permian forms a largely impermeable base to the aquifer which extends to about 300 mbgl at its deepest point in the east. The Mercia Mudstone overlies the Sherwood Sandstone in the east, forming an effective confining horizon (21). Rates of vertical movement for recharge in the Triassic sandstone calculated using chloride profiles in the unsaturated zone from the West Midlands are about 2.3 m/a (22). This equates to travel times of between three and seven years in the unsaturated zone. Abstraction significantly affects the groundwater flow in the region, but under natural conditions flow is in an easterly direction. Hydraulic conductivities for the Sherwood Sandstone have a median value of 2.1 m/a and a range of 0.35-4.7 m/a (23). River/aquifer interactions, localised urban leakage, interaction with drainage networks and the underlying formations are all important components of the regional water balance.

Groundwater Sampling and Analysis

A total of 14 shallow monitoring sites were sampled over the 22-month period between January 2002 and November 2003. For the first two and a half months the sampling frequency was bi-monthly; thereafter it was monthly. In the initial phase of monitoring a network of nine sites was used; a later phase used a network of ten sites with new sites being added to the network as they became available. The analytical suites included compounds which are more commonly used in the UK and found in groundwaters, relatively few insecticidal compounds are used in the UK and this was reflected in the analytical suites used. A total of forty compounds were screened and the analysis was carried out by SAC scientific. Table 2 details the four analytical suites used.

RESULTS

Pesticides Occurrence in the Shallow Aquifer

Spatial Variability Across the Monitoring Network

The pesticides detected, maximum, mean and percentages of positives exceeding the PCV of 0.1 μg/L for individual pesticides in drinking water (9) observed during the course of the groundwater monitoring are shown in Table 3. A total of 294 positive detections were made. Of these positive detections 34% were detected in excess of the PCV for individual pesticides. Pesticides were detected in 11 of the boreholes, and in 8 of the 14 boreholes pesticide concentrations exceeded the PCV on at least one occasion. The six most frequently detected pesticides have been observed at concentrations exceeding the PCV, and for four of these the mean value also exceeds the PCV. Half of the pesticides have been detected at more than one site, and on more than one occasion, with MCPP being the most commonly detected compound, found at 9 different sites. Isoproturon, chlorotoluron, atrazine and simazine were all found at four or more sites. The high occurrence of herbicidal compounds could be a reflection of the bias in analytical screening, only two insecticides were screened for, and although this does not mean that other pesticides are not present in the groundwater it is thought very unlikely.

The variations in pesticide detection across the study area are shown in Table 4. The data are presented in order of decreasing numbers of positive detections per site. Positive detections were made at 11 of the 14 sites, indicating pollution in the shallow part of the aquifer is widespread and not confined to a few isolated locations. At 8 of the sites a positive detection was made on at least every other sampling occasion. This shows the value of a regular and frequent sampling programme. There is some relationship between the frequency of detections and the magnitude of those detections, with S9 being the notable exception to this having frequent detections at concentrations below the PCV. Sites S3, S2, S5, S13, and S14 all show frequent detections with a significant proportion exceeding the PCV.

Temporal Variations in Pesticides within the Shallow Aquifer

Temporal Variability Across the Monitoring Network

The monitoring programme has permitted an assessment of temporal trends and produced a unique pesticide dataset in terms of its length, frequency and regional cover. While the data series presented below are suitable for the assessment of trends in terms of their time span and sampling interval (24), it is important to emphasise that this series fulfils only the minimum requirements in most cases. In addition, the autumn of 2003 was atypical in terms of rainfall, with only 120 mm of rainfall compared to a ten-year mean of 185 mm, and only a longer time series would establish the significance of this for pesticide occurrence in groundwater. Trends in groundwater pesticide concentrations are dependent on a number of variables such as timings and rates of application, degradation, transport through the unsaturated zone, recharge, soil characteristics and geology.

It might be reasonable to suggest that variations in pesticide occurrence could be explained in part by recharge. With greater recharge the greater the pesticide flux down the profile, from the unsaturated zone to the saturated zone. Rainfall is the most important recharge input and is a good indicator of potential recharge. Potential recharge is also dependant on other factors such as evaporation losses, irrigation and runoff, and while it is a good estimation of recharge to the aquifer it must be understood within the geological context.

Given the difficulties in comparing sites across the study area due to differences in pesticide concentrations and types, the changes in positive detections per sample (PPS) have been calculated, as well as the PPS > PCV. PPS is given as the number of positive detections on a given date divided by the number of sites, only those sites which were sampled throughout the entire monitoring period were included. These are shown with monthly rainfall in Figure 4. The PPS series shows no clear seasonal pattern, however there is a peak in September 2002 and a steady increase from July to October of 2003 which corresponds with the period of highest rainfall in the autumn. There is a clearer seasonal pattern if only detects > PCV are considered, this is a reflection of the poorer analytical precision at concentrations close to the detection limit, and highlights the obvious limitations in interpreting such poorly resolved data.

Temporal Variability at Individual Sites

Temporal variations in pesticide concentrations from five sites are shown in Figure 5. These were selected since they show the most frequently detected pesticides, enabling an assessment of temporal trends to be made. The main points are summarised below:

- At some sites, e.g. S1, S3 and possibly S14, the same temporal trends were observed for different pesticides, while S9 different pesticides showed different temporal trends. The former could be due to applications of multiple pesticides from a single source, be it point or diffuse. The latter may be due to multiple sources of pesticides or the relative proximity of the sources, or because some compounds were detected at concentrations close to or below the detection limit.
- Some pesticides exhibit erratic detections e.g. MCPP at S9, while others were detected throughout the monitoring programme, e.g. bentazone at site

9. This could again be due to the proximity of the source, and the initial source concentration.

- The magnitude of maximum concentrations varies greatly between sites, suggesting differences in pesticide sources. At S5 MCPP was detected consistently above 2 μg/L, well above the concentration normally associated with diffuse pesticide usage from arable agriculture (3), suggesting a point source such as a soakaway. At S1 detections were all below 0.2 μg/L suggesting a more diffuse source of pollution. At S3 MCPP was consistently detected in high concentration, possibly from a landfill, and low detections of bentazone and clopyralid were found, most likley from diffuse agricultural sources.
- There is no consistent increasing or decreasing trend across different sites. Sites S9 and S14 show an upward trend for bentazone and atrazine, while S3 shows a downward trend for MCPP.
- There is some consistency in the temporal trends at different sites. Four of the five sites show peaks in pesticide concentrations during the autumn, and four sites show peaks in early spring. The coincidence of these peaks may be significant and could point to a systematic influence on the occurrence of pesticides across the area for a range of pesticides. This is likely to be the result of a complex relationship involving recharge, irrigation, pesticide applications, chemical and physical aquifer properties as well as the chemical properties of different pesticide compounds.

Pesticide metabolites have been shown to occur within groundwaters at higher concentrations than parent compounds (4), and have also been shown to help in understanding spatial and temporal trends in groundwater (25). While considering metabolites was beyond the scope of this study it is worth noting that this needs to be investigated further. Pesticide metabolites may be considered as pollutants under the proposed WFD Daughter Directive relating to the protection of groundwater (7).

Pesticide Pollution at Depth in the Aquifer

While shallow boreholes are the best indicators of pesticide loading to the aquifer, some deeper boreholes penetrating >100 m and cased to 30 mbgl have also shown an upturn in pesticide concentrations. Total pesticide concentrations from three contaminated boreholes sampled between 2000 and 2004 are shown in Figure 6. The composition of the pesticide contamination remained fairly constant throughout the sampling period in each case. At S15 mecoprop, bentazone and isoproturon account for >90% of the total pesticide detected. Atrazine accounted for >90% of the detections at S16 and S17, although simazine was also detected on a number of occasions.

All three series show an upward trend between July 2000 and October 2002, with the maximum total pesticide concentrations during the recharge period of 2002 for two of them. S15 and S16 show the same seasonal trends, which mirror those observed in the shallow network. S17 is located close to S14, and both sites are contaminated with significant concentrations of atrazine, and occasional concentrations of simazine and propazine. Site S17 shows a more suppressed temporal variation, and much lower detections. This suggests the same source of contamination at both sites, possibly the nearby railway line, but the lower detections at S17 may be due to mixing of a shallow pollution source with deeper less contaminated groundwaters.

DISCUSSION

Pesticide occurrence does show some correlation with landuse, Table 5 details the landuse/pesticide source and pesticides detected within the shallow monitoring network. The widespread occurrence of MCPP, isoproturon, chlorotoluron and atrazine reflects the predominantly arable landuse as a diffuse source of pesticide pollution. Dicamba and was detected at a golf course, and atrazine, simazine, propazine and terbutryn were detected near a railway. Sites that had a semi-natural/suburban landuse generally showed lower positive detections per sample.

Poor disposal practice, spillages, run-off and losses from washdown areas are cited as potential sources for pesticide pollution (26). The rapid transport of pesticides to the aquifer by way of soakaways or drains; from washings, disposal or spillages, could explain the occurrence of some high pesticide concentrations within the groundwater system. Detections at different sites cannot be explained simply in terms of geographical location. The drift cover of the area is highly heterogeneous, making it difficult to relate pesticide occurrence in terms of aquifer vulnerability due to different recharge and flow-path scenarios. The five most commonly detected pesticides, MCPP, bentazone, isoproturon, atrazine and clopyralid are all classified as having a high potential to leach to the groundwater (17,27). This suggests that the mobility and persistence of different compounds in the soil and aquifer system may be controlling their occurrence in groundwater.

Pesticide usage data are not available on a local scale for most sites, making it impossible to explain occurrence in terms of pesticide application. Historical records of pesticide usage were only available for three sites for a limited period. No clear relationship between usage and occurrence in groundwater was found, possibly reflecting the travel time in the unsaturated zone, the rapid degradation of some pesticides within the shallow aquifer system or the accuracy of the records. Due to crop rotation and changing pesticide applications, longer records (at least 5-10 years) of pesticide usage may be needed to fully relate occurrence in groundwater to usage.

A good positive correlation between rainfall and PPS>PCV also exists, although the changes in pesticide detections are unlikely to be a direct result of recharge from the same period, and may be derived from several factors such as changes in groundwater level, timing of pesticide applications, and irrigation rates. Potential recharge, calculated using soil moisture deficits, occurred between October 2002 and February in 2003 and coincides with a drop in pesticide detections. The relationship between PPS and rainfall does break down in autumn 2003, which had exceptionally low rainfall. There was however significant agricultural irrigation during this time in response to the lack of rainfall, which could account for the continued rise in pesticide detections. While there is no correlation with potential recharge, several sites do show peaks in pesticide detections during the recharge period. However, overall these highs are small in relation to those observed in autumn.

Since the data collection interval is very irregular for the for the deep borehole series, the usefulness of the data for trend analysis is limited. Regular monitoring of raw water is essential if future trends in pesticide detections in deeper groundwaters are to be understood. The deterioration of water quality in a number of boreholes at depth in the aquifer is a cause for some concern, and some general observations about the trends can be made as follows:

- All of these sites can be described as unconfined. The overlying drift deposits comprise sands and gravels with high transmissivities, and therefore the aquifer is vulnerable.
- The upward trend between 2000-2002 and downward trend during 2003 could be the direct result of a pollution front related to the unusually high recharge during the autumn-winter of 2000-2001. Contaminated water moving through the unsaturated zone mixes with water in the saturated

zone, producing a steady increase and then decrease in pesticide concentrations. Combined with this, the rising water levels would also contribute to the overall response in pesticide detections.

- The agreement between the trends from the shallow private boreholes and those from S15 and S16 between 2002 and 2003 could suggest that the same factors, e.g. recharge, timing of applications, are also influencing pesticide detections in deeper groundwaters, where the aquifer is unconfined.
- In other situations the dilution caused by mixing with older waters or soil properties and thickness could enable greater dilution/degradation of the pesticide flux.

CONCLUSIONS

1. Significant concentrations of pesticides have been detected in the shallow part of the aquifer, showing the potential for pesticides to be leached from the soil and transported to depth. The variable concentrations detected implicate both point and diffuse sources of pollution. Metabolites might also be found in detectable concentrations, and could become a future problem for abstractors if they are included as pollutants within future legislation.
2. Pesticide occurrence correlates to some extent with landuse. Atrazine, terbutryn and propazine were all found in close proximity to a railway, dicamba and benazolin were found at a golf course and MCPP, bentazone and isoproturon were found in areas of arable agriculture.
3. The extended period of high frequency sampling enabled temporal patterns to become evident at some individual sites. While the magnitude of the maximum

pesticide concentrations varies between sites probably reflecting proximity to pollution sources and different antecedent conditions, the coincidence of these peaks at different sites suggests there may be common influences on the occurrence of pesticides in groundwater.

4. No consistent upward or downward trend was observed within the shallow borehole monitoring network. Any predictions in terms of long-term pesticide trends is made difficult because the unusually low rainfall during the autumn of 2003. This could have had a significant effect on the occurrence of pesticides during this period.
5. Due to apparent seasonal fluctuations, longer-term (5-10 years) monitoring is required to establish trends in pesticide detections within the aquifer and properly assess processes which influence pesticide occurrence in groundwater.
6. The apparently accelerated rate of deterioration in water quality within the deeper aquifer must be a cause for concern and may have implications for the future management of this regionally significant water resource, as well as for other aquifers within the UK with similar land-use settings and vulnerability.

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Table 1. Examples of pesticides, and relation to landuse

Landuse/Source	Area Treated	Frequency	Examples
Arable Agriculture	Fields	Annual/bi-annual[+]	Isoproturon, MCPP, atrazine*
Urban (amenity use)	Paths/kerbs	Annual/bi-annual	Imazapyr, 2,4-D, glyphosate
Golf Course	Green/paths	Bi-annual	2,4-D, dicamba,
Landfill	-	Continual/episodic	Various (MCPP, atrazine, 2,4-D)
Railway	Tracks/stations	Annual	Atrazine*, simazine*, diuron, glyphosate
Motorway	Central reservation	Annual	2,4-D, Picloram, glyphosate

* Banned from non-crop use from 1993, [+] Frequency is compound/crop specific

Figure 2: A breakdown of the compounds covered in each of the four analytical suites

Phenoxyacidic	Carbamates	Triazines	Phenylurea
2,3,6-TBA	Carbaryl	Atrazine	Carbetamide*
2,4,5-T	Carbetamide*	Prometryn	Chlorotoluron
2,4-D	Chloropropham	Propazine	Diuron
2,4-DB	Methiocarb	Simazine	Isoproturon
4-CPA	Pirimicarb	Terbutryn	Linuron
Benazolin	Propham	Terbutylazine	Methabenzthiazuron
Bentazone		Trietazine	Monuron
Bromoxynil			
Clopyralid			
Dicamba			
Dichlorprop			
Diclofop			
Fenoprop			
Flamprop			
Ioxynil			
MCPA			
MCPB			
Mecoprop			
Pentachlorophenol			
Picloram			
Triclopyr			

*Carbentamide is in both the carbamates and phenylurea suites

Table 3: Summary statistics for pesticides detected on more than one occasion

Pesticide	Positives	Max Concentration	Mean* Concentration	% n>PCV	Sites
MCPP(H)	72	7.1	2.143	63	9
Bentazone (H)	45	0.12	0.057	7	2
Isoproturon (H)	42	1.2	0.345	48	5
Atrazine (H)	40	4.2	0.585	55	4
Clopyralid (H)	25	0.082	0.048	0	3
Benazolin (H)	20	0.18	0.105	60	1
Dicamba (H)	7	0.052	0.041	0	1
Chlorotoluron (H)	7	0.059	0.048	0	5
Propazine (H)	7	0.14	0.055	14	2
Simazine (H)	6	0.062	0.030	0	4
Pentachlorophenol (H)	6	0.041	0.028	0	3
Terbutryn (H)	4	0.13	0.077	25	1
Dichlorprop (H)	2	0.048	0.040	0	2
MCPA (H)	2	0.056	0.045	0	1
Pirimicarb (I)	2	0.37	0.201	50	2

All concentrations, max and mean, in µg/L * Mean of positive detections, Herbicide (H), Insecticide (I)

Table 4: Pesticide detections from all 14 sites in the shallow aquifer

Site	+Ves	Times Sampled	+Ves Per Sample	+Ves Per sample>PCV
S3	86	22	3.9	1.86
S2	56	24	2.3	0.5
S9	52	22	2.4	0.09
S14	37	20	1.9	0.95
S5	25	21	1.2	1
S13	12	12	1.0	0.33
S4	8	9	0.9	0
S1	6	7	0.9	0
S7	5	24	0.2	0.04
S12	4	16	0.3	0.06
S6	4	24	0.2	0
S11	0	6	-	-
S8	0	6	-	-
S10	0	7	-	-

Table 5: Landuse, possible pesticide sources and most frequently detected pesticides from the shallow monitoring sites

Site	Landuse/possible contaminant source	Pesticides detected * (PPS)
1	Semi-natural	Pentachlorophenol, MCPP, simazine (0.9)
2	Golf course, arable	Benazolin, atrazine, dicamba (2.3)
3	Arable, landfill	MCPP, bentazone, clopyralid (3.9)
4	Semi-natural	MCPP, isoproturon, clopyralid (0.9)
5	Arable, nursery	MCPP, atrazine, diuron (1.2)
6	Arable	MCPP, MCPA (0.2)
7	Arable	Isoproturon, dicloprop, chlorotoluron (0.2)
8	Semi-natural	-
9	Arable, landfill	Bentazone, Isoproturon, MCPP (2.4)
10	Arable	-
11	Suburban, industrial	-
12	Semi-natural, arable	Chlorotoluron, isoproturon, MCPP (0.3)
13 +	Railway, semi-natural	Atrazine, propazine, MCPP (1.0)
14 +	Railway, semi-natural	Atrazine, propazine, MCPP (1.9)

* Three most frequently detected pesticides, in order of decreasing frequency (normalised positive detections per sample), + Simazine and terbutryn also detected at these sites

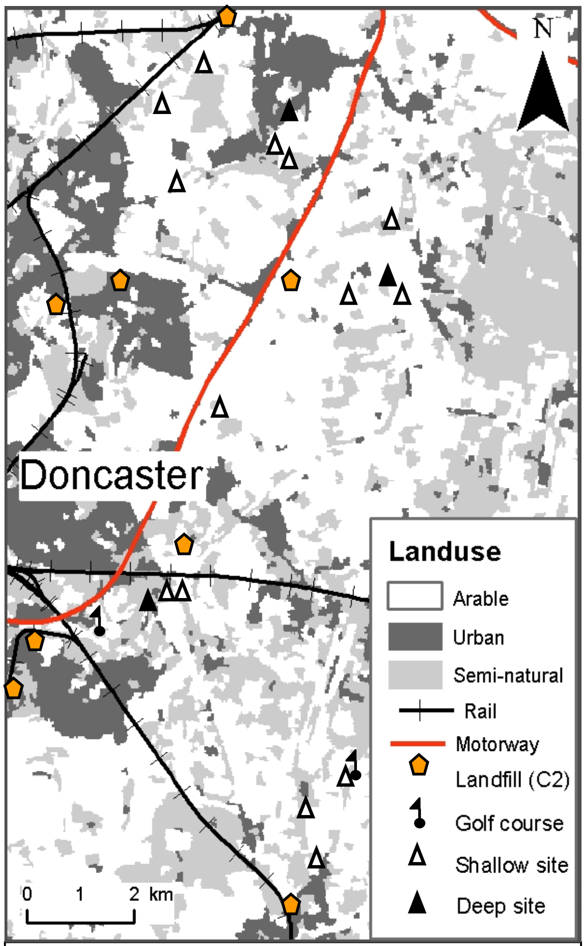

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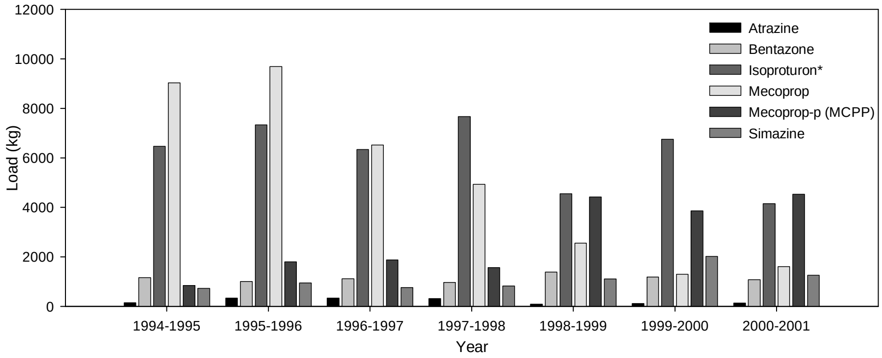
Figure 1: Sampling locations in relation to landuse



*Isoproturon values are /5

Figure 2 Annual agricultural applications of key herbicides over Doncaster area from 1994 – 2001 (data supplied by Produce Studies)

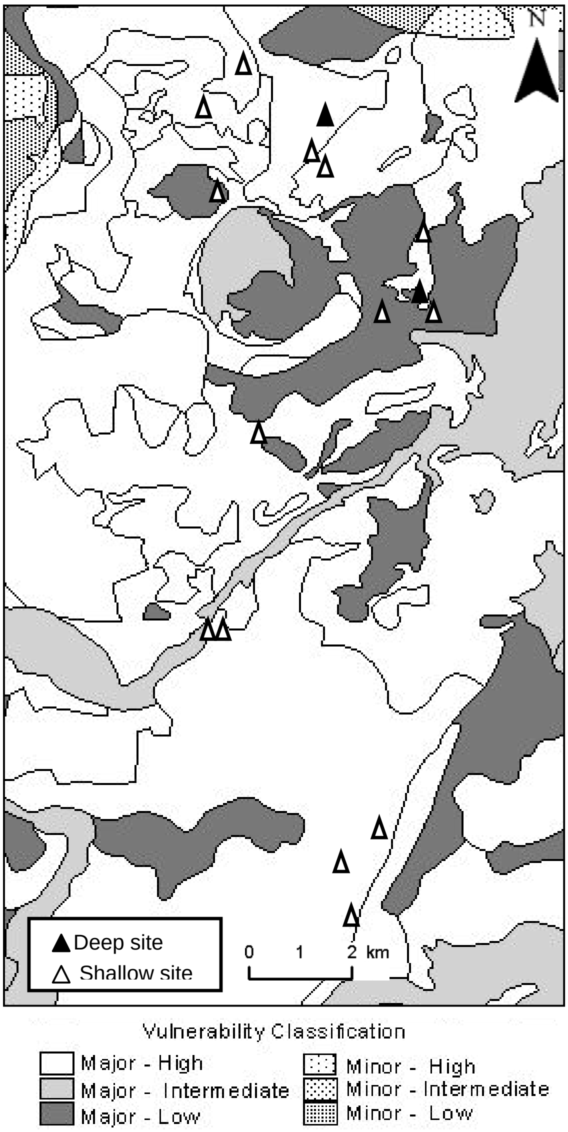


Figure 3: Aquifer Vulnerability classification (after NRA, 1995)

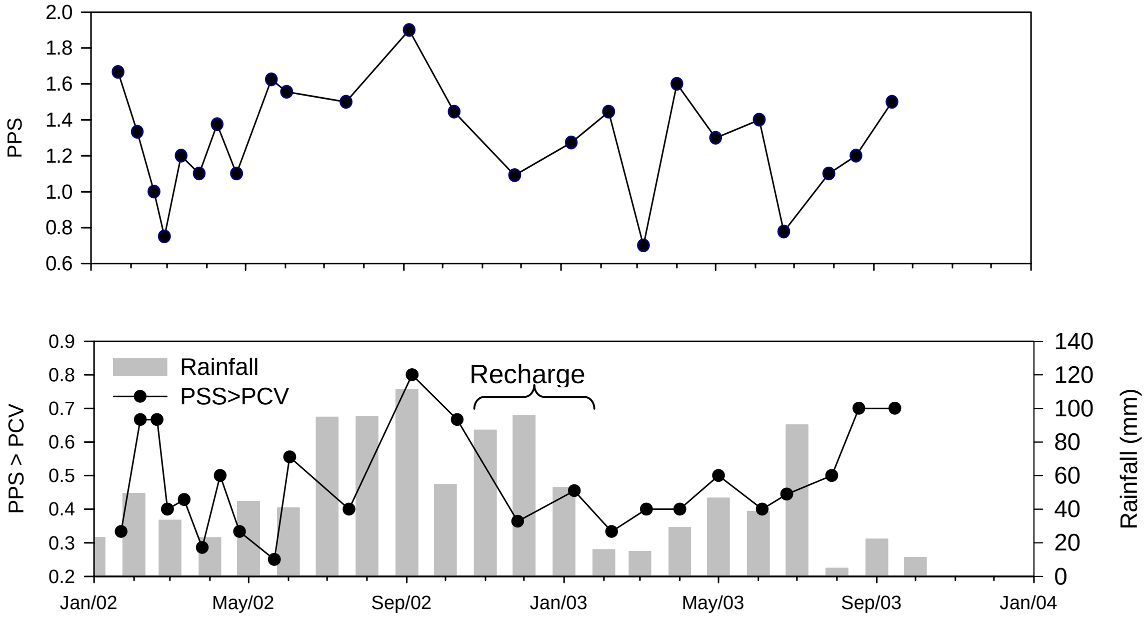
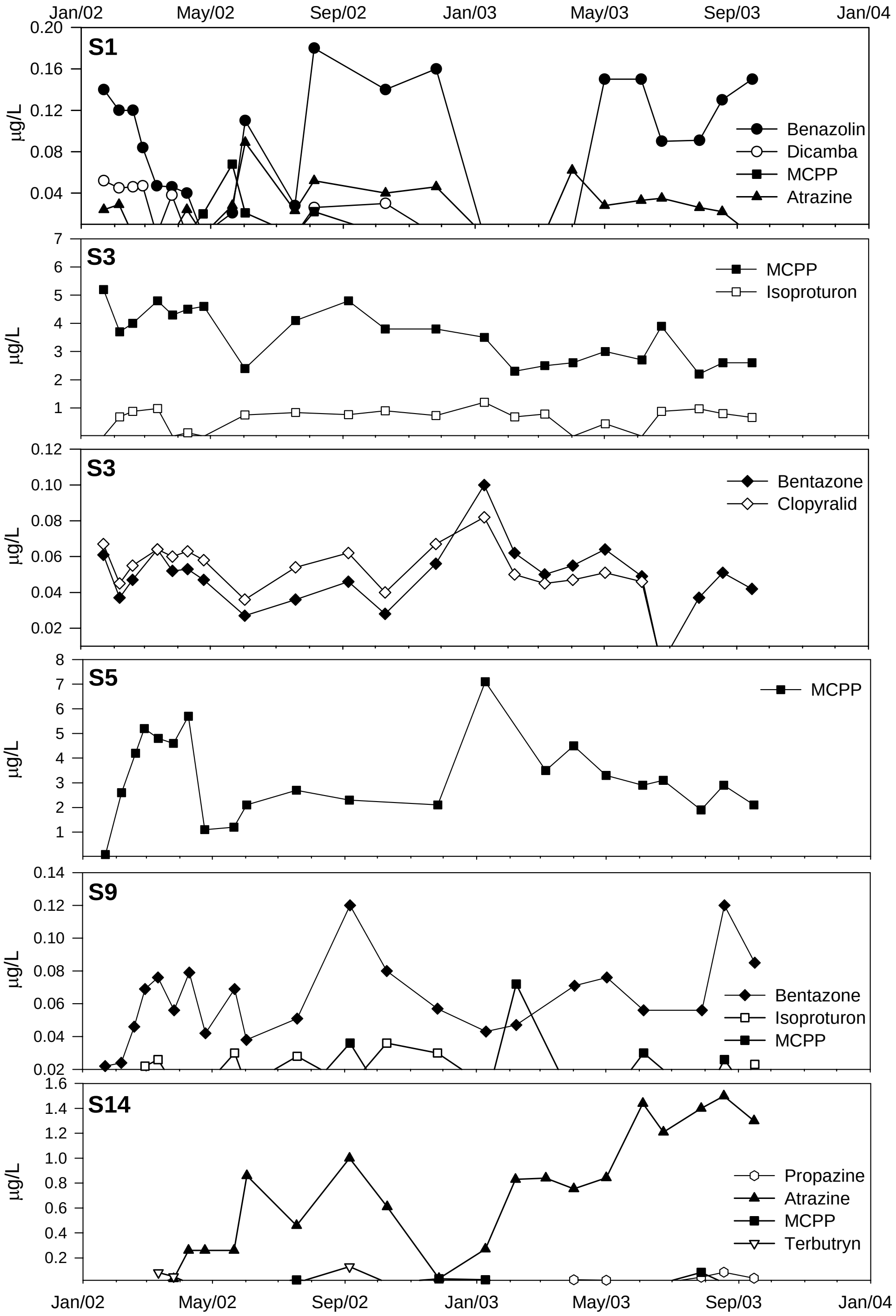


Figure 4: Changes in positive detections per sampling (PPS), PPS > PCV, and rainfall



Scales used on the y-axis (µg/L) vary between plots

Figure 5: Temporal variations in pesticide detections at selected sites in the shallow aquifer.

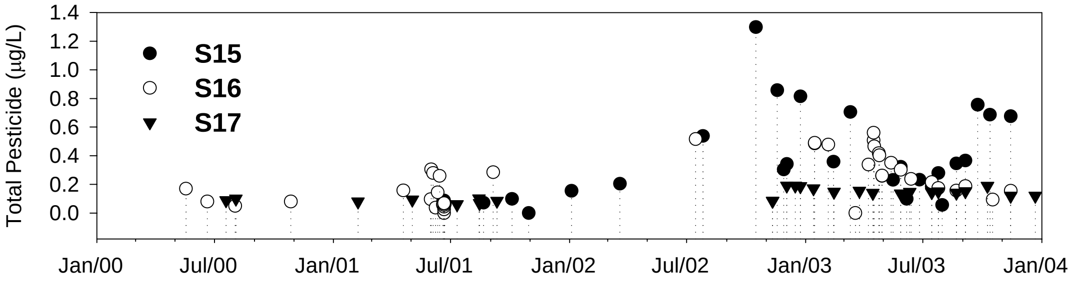


Figure 6: Temporal variations in total pesticide detections at selected boreholes that penetrate deeper into the aquifer (cased to >30 mbgl)