Table 1 Summary of the hydrogeological setting of the study sites.

	ASM	AWC	LEC	WON	CPN
Area	Hampshire	Hampshire	Hampshire	Hampshire	Oxfordshire
Aquifer	Upper Chalk	Upper Chalk	Upper Chalk	Upper Chalk	Lower Chalk
Site topography	Sloping field adjacent to valley bottom	Sloping field adjacent to valley bottom	Steeply sloping valley flank	Flatter ground on interfluve	Flatter ground on interfluve
Soil thickness (m)	0.3–0.8	0.4–0.5	0.2 soil; 0.7 subsoil	0.6–0.9	0.5–0.6
Unsaturated zone	Soft ‘lumpy’ chalk	Soft weathered chalk	Broken chalk and flints passing into chalk with few fractures	Weathered chalk to 3.4 m with more solid chalk below	Soft well-fractured chalk with few flints
Depth to water (m)	3–5	7–9	3–4.5	4–6 at bottom of field	>25

Table 2 Summary of scientific tasks and methods employed.

Scientific task	Method employed	New development or adaptation
Determine pesticide residues in soil and chalk unsaturated zone	Drill and retrieve core samples for solid and liquid extractions	Use of ELISA for porewater pesticides
Detect arrival of pesticides at the water table	Regular groundwater sampling from observation boreholes completed just below water table	Multi-level hanging sampler and automatic pumped sampler
Investigate mechanisms of water movement in the unsaturated zone	Installation of soil moisture instrumentation to 3 m depth. Soil and chalk inspection pit	Integration of structural geology and hydrology
Confirm origin of pesticide in groundwater	Application of pesticide chlortoluron not previously used at site	
Investigate solute movement in deep unsaturated zone	Laboratory chalk columns. Shallow coring in field, tracer test	New method developed; bromide tracer test
Evaluate sorption as retention mechanism	Column and batch experiments	
Evaluate pesticide degradation potential of aquifer material compared with that of soil	Laboratory microcosms using chalk and groundwater	Method refined in project

Table 3 Summary of unsaturated zone sampling methods.

Materialsampled	Objective	Approach	Detailed methoddescription
Soil	Determine isoproturon residues after application	Weekly from top 0.02 m and occasionally to 0.2 m; methanol extraction for pesticide	Johnson *et al*. 2001
Solid chalk	Determine vertical distribution of pesticide residues	Subsamples from cores at regular depth intervals; methanol extraction	Chilton *et al*. 1993; Gooddy *et al*. 2001
	Determine bacterial numbers	Scraping with sterile spatula from centre of cores	Johnson *et al*. 1998
Chalk porewaters	Determine vertical distribution of dissolved pesticides	Centrifuge extraction of water from crushed core for analysis by HPLC and ELISA	Chilton *et al*. 1993; Gooddy *et al*. 2001
	Determine transport of applied bromide tracer	Centrifuge extraction of water from crushed core for chemical analysis	Haria *et al*. 2003
	Examine unsaturated zone transport mechanisms	Centrifuge extraction of water from crushed core for analysis for nitrate and chloride	Gooddy *et al*. 2001

Table 4 Summary of pesticide analytical methods used in study.

Sample type	Compound	Method	Detection limits	Detailed description
Soil	Isoproturon	Methanol extraction and HPLC	0.09–0.23 (μg kg^{-1})	Johnson *et al*. 2001
Solid chalk	Isoproturon	Methanol extraction and HPLC	0.09–0.23 (μg kg^{-1})	Johnson *et al*. 2001
	Chlortoluron			
Porewater	Isoproturon	ELISA	0.01(μg l^{-1})	Gooddy *et al*. 2001
		Methanol extraction and HPLC		
Pumped groundwater	Isoproturon	Solid-phase extraction and HPLC	0.02–0.1 (μg l^{-1})	Gooddy *et al*. 2001; Johnson *et al*. 2001
Chlortoluron		0.02–0.04 (μg l^{-1})		
	Atrazine		0.05 (μg l^{-1})	
Batch sorption	Isoproturon	Filtration (0.45 μm) and HPLC	0.01 (μg l^{-1})	Besien *et al*. 2000
Chalk columns	Isoproturon	Methanol extraction and HPLC	0.01 (μg l^{-1})	Besien *et al*. 2000
Microcosms	Isoproturon	Filtration (0.2 μm) and HPLC	10 (μg l^{-1})	Hughes *et al*. 1995; Johnson *et al*. 1998, 2000
	Mecoprop	Solid-phase extraction and HPLC	1 (μg l^{-1})	

Table 5 Summary of laboratory studies.

Task	Method	Detailed description
Enumeration of bacteria	Scraping from centre of core and assessments of the number of viable aerobic, heterotrophic bacteria	Johnson *et al*. 1998
Degradation of pesticides in microcosms	Fresh crushed chalk core and groundwater. Autoclaved material as control. Mecoprop spike added at 50 µg l^{-1}, Isoproturon spike added at 100 µg l^{-1}, incubated at 20 °C in the dark, without shaking for 60 days for mecoprop and up to 300 days for isoproturon	Hughes *et al*. 1995; Johnson *et al*. 1998
Chalk metabolic potential	Chalk microcosm with radiolabelled acetate	
Degradation of pesticides in unsaturated columns	Undisturbed chalk columns irrigated under tension and isoproturon and bromide tracer spikes applied. Unsaturated conditions simulated by applying a suction of 1 kPa to the base of the columns, and tensiometers installed horizontally into the chalk used to monitor and maintain unsaturated conditions	Besien *et al*. 2000
Batch sorption	Cores from same boreholes as the column experiments	Besien *et al*. 2000

Table 6 Summary of observed unsaturated zone pesticide concentrations from early part of study.

Site	Aquifer	Pesticide	Monthssinceapplied	Depth(m)	Solid					
			Samples(no. positive)	Concentration (μg kg^{-1})		Concentration (μg l^{-1})				
				Mean	Range	Mean	Range			
This study										
LEC	Chalk	Isoproturon	11	10	11 (1)	<0.5	<0.5–0.5	11 (0)	—	<0.5
WON	Chalk	Isoproturon	31	10	10 (1)	<0.5	<0.5–1	10 (0)	—	<0.5
AWC	Chalk	Isoproturon	13	10	9 (1)	<0.5	<0.5–1	9 (3)	—	<0.5–3.8
ASM	Chalk	Atrazine	20	5	8 (8)	0.3	0.11–0.48	14 (14)	3.65	0.1–6.7
CPNa	Chalk	Atrazine	3	5	15 (2)	0.1	<0.1–0.47	8 (7)	0.59	<0.02–3.38
CPNb	Chalk	Atrazine	3	5	16 (10)	0.74	<0.1–8.6	9 (9)	0.76	0.21–1.86
Clark et al. *(1995)*										
Assarts Farm	Sherwood Sandstone	Mecoprop	—	10	10 (5)	<0.2	<0.05–0.3	—	—	—
CPN	Chalk	Atrazine	—	11	8 (8)	<0.5	0.75	15 (15)	0.54	0.2–0.95
Bishopfield Farm	Sandstone	Trietazine	—	10	17 (5)	<0.1	<0.05–3.0	—	—	—
	Sandstone	Simazine/Trietazine	—	10	—	—	—	18 (17)	0.14	<0.01–0.47

Table 7 Summary of saturated zone pesticide concentrations.

Site	Period ofsampling	Pesticide	Range of depthto water (m)	No ofsamples	No ofpositivedetections	Positivedetections(%)	Concentration (µg l^{-1})	
		Median	Maximum					
LEC	2/92–3/93	Isoproturon	2.9–4.4	11	1	9	<0.05	0.05
AWC	4/92–3/95	Isoproturon	6.9–9.0	24	12	50	<0.05	0.34
ASM	4/92–3/95	Atrazine	2.1–7.9	29	11	38	<0.1	0.84
WON4	2/92–3/98	Isoproturon	0.6–6.8	44	5	11	<0.05	0.23
	10/96–3/98	Chlortoluron		21	9	43	<0.04	0.12
WON5	11/95–6/98	Isoproturon	1–6 approx.	97	71	73	0.15	0.6
	10/96–6/98	Chlortoluron		75	47	63	0.13	0.8
WON15	1/98–3/98	Isoproturon	1–6 approx.	36	29	81	0.13	0.4
		Chlortoluron		36	23	64	0.09	0.18
WON6	10/96–4/98	Isoproturon	7.8–9.6	13	2	15	<0.05	0.13
		Chlortoluron		8	5	63	0.08	0.15
WON7	10/96–4/98	Isoproturon	13.4–17.4	17	1	6	<0.05	0.1
		Chlortoluron		13	2	15	<0.05	0.15

Table 8 Periods where conditions favoured preferential flow at Site WON 4.

Season	Periods when matric potential at 3 mdepth was > –5 kPa
1995–1996	27 November 1995–9 December 1995
	23 December 1995–5 January 1996
	9 January 1996–3 February 1996
	27 February 1996–9 March 1996
1996–1997	8 December 1996–10 December 1996
	25 February 1997–6 March 1997

Table 9 Estimated isoproturon half-lives for 100 µg l^{-1} at 20 °C (and range of values) for groundwater samples taken from different boreholes at different times.

Borehole	May 1995	November 1995	November 1996	January 1997	March 1998
WON4	7 days(7–20 days)	97 days (92–102 days)	104 days(all 104 days)	None after 149 days	None after 202 days
WON5	n.d.	362 days (52–575 days)	n.d.	387 days (227–641 days)	575 days (239–850 days)
WON6	n.d.	n.d.	n.d.	None after 149 days	280 days (239–306 days)
WON7	n.d.	n.d.	n.d.	174 days (138–227 days)	228 days (212–247 days)

Table 10 Crop rotation and pesticide usage at site WON.

Year	Crop	Number ofcompounds	Number ofapplications
1985	Winter barley	5	3
1986	Combining peas	4	2
1987	Winter wheat	7	3
1988	Winter wheat	9	5
1989	Winter barley	15	3
1990	Spring turnips and barley	7	2
1991	Grass for seed	2	1
1992	Peas	8	4
1993	Winter wheat	7	3
1994	Winter wheat	10	5
1995	Winter barley	16	5
Total number of compounds			