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## Rainfall and runoff water quality of the Pang and Lambourn, tributaries of the River Thames, south-eastern England

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### Abstract

The water quality of rainfall and runoff is described for two catchments of two tributaries of the River Thames, the Pang and Lambourn. Rainfall chemistry is variable and concentrations of most determinands decrease with increasing volume of catch probably due to 'wash out' processes. Two rainfall sites have been monitored, one for each catchment. The rainfall site on the Lambourn shows higher chemical concentrations than the one for the Pang which probably reflects higher amounts of local inputs from agricultural activity. Rainfall quality data at a long-term rainfall site on the Pang (UK National Air Quality Archive) shows chemistries similar to that for the Lambourn site, but with some clear differences. Rainfall chemistries show considerable variation on an event-to-event basis. Average water quality concentrations and flow-weighted concentrations as well as fluxes vary across the sites, typically by about 30%. Stream chemistry is much less variable due to the main source of water coming from aquifer sources of high storage. The relationship between rainfall and runoff chemistry at the catchment outlet is described in terms of the relative proportions of atmospheric and within-catchment sources. Remarkably, in view of the quantity of agricultural and sewage inputs to the streams, the catchments appear to be retaining both P and N.

**Keywords:** water quality, nitrate, ammonium, phosphorus, ammonia, nitrogen dioxide, pH, alkalinity, nutrients, trace metals, rainfall, river, Pang, Lambourn, LOCAR

### Introduction

Interest in the water quality functioning of lowland UK river systems has grown over the last ten or more years with earlier initiatives such as the Land Ocean Interaction Study (LOIS) (Leeks and Jarvie, 1998; Neal *et al.*, 2003) and new initiatives such as LOCAR (Lowland Catchment Research: [www.nerc.ac.uk/funding/thematics/locar/](http://www.nerc.ac.uk/funding/thematics/locar/)). Such initiatives have been undertaken to monitor the environment, understand the key processes operating and to model the dynamics of catchment systems in relation to environmental science and environmental management. The issues covered are of national and international significance within programmes such as the Land Ocean Interaction Study (LOIS), the study of European Catchments (EUROCAT), European Land Ocean Interaction Study (ELOISE), and the Land Ocean Interaction in the Coastal Zone study (LOICZ),

which extend to the global level within the International Geosphere Biosphere Programme (IGBP) (Leeks and Jarvie, 1998; Cave *et al.*, 2003).

Within the UK there is a growing emphasis on lowland river systems because the lowlands are major population and industrial centres and have the highest amount and intensity of agricultural activity; all of this leads to major issues of surface water pollution both in the context of riverine management and pollutant fluxes to the sea (Robson and Neal, 1997; Jarvie *et al.*, 1997). Further, within lowland systems there are issues of the effects of nutrient discharges from urbanisation, industry and agriculture on biological status and riverine health as well as on the legal and environmental management options for improvement (Jarvie *et al.*, 1998; Mainstone and Parr, 2002; Withers and Lord, 2002).

While within the LOIS programme there was a range of interests on rural, agricultural and urban/industrial systems, there has remained until recently within the LOCAR project less emphasis on catchment research for agricultural systems. Within LOCAR, the remit is to undertake interdisciplinary programmes of integrated hydro-environmental research relating to the input-storage-discharge cycle and in-stream, riparian and wetland habitats within groundwater-dominated systems. Key to LOCAR has been (a) the establishment of field research facilities in three contrasting permeable lowland catchments, the Frome/Piddle in Dorset, the Pang/Lambourn in Berkshire and the Tern in Shropshire and (b) determination of the extent of these types of groundwater system throughout the UK.

This paper presents an overview on the water quality of rainfall and stream runoff from one of the main LOCAR study areas, the Pang/Lambourn, from the point of view of input-output relationships. This work is based on over a year's monitoring across the catchments and links to longer term studies by CEH Wallingford on examining water quality changes within the upper Thames basin (Neal *et al.*, 2000a) at a time of climatic instability (Marsh and Sanderson, 1997). It includes water quality data for rainfall which is often overlooked in lowland catchment research but which can show up highly significant inputs (Smith *et al.*, 1997) and it draws upon rainfall quality data from the UK National Air Quality Archive (Vincent *et al.*, 1996). It also includes an estimate of dry deposition of some oxidised and reduced nitrogen species. This was achieved using diffusion tubes, a low-cost, well established technique for measuring gaseous concentrations of nitrogen dioxide (NO<sub>2</sub>) and ammonia (NH<sub>3</sub>) (Atkins *et al.*, 1986; Sutton *et al.*, 2001).

The paper provides a backdrop for new modelling and

process based studies on the Pang/Lambourn, and complements earlier monitoring and modelling studies for these rivers, the Kennet and main stem of the upper River Thames, into which these tributaries discharge (Neal *et al.*, 2003).

## Study Area

### LOCATION AND GENERAL CATCHMENT CHARACTERISTICS

The Pang and Lambourn are tributaries of the River Thames, the principal river in south-east England. Their catchments are adjacent and their areas are about 171 and 234 km<sup>2</sup>, for the Pang and Lambourn respectively (Fig. 1). The Pang has its source towards the east of its catchment and it joins with the Thames near the town of Pangbourne. The Lambourn drains east-south-eastward from spring sources at the village of Lambourn and enters the River Kennet at Newbury, which in turn drains into the Thames near Reading to the east. Both catchments are located approximately 90 km from the south coast and the Thames estuary to the east. Within both catchments, land-use is largely rural to moderately intensive farming. The population is relatively low, within villages, small hamlets and farming communities in the surrounding countryside, apart from the towns of Pangbourne and Newbury at their confluence with the Thames and Kennet respectively.

The underlying geology across the area is predominantly of Cretaceous Chalk. The Pang has only one significant stream input, the Bourne, which drains clays of Eocene age while the Lambourn also has only one significant tributary input, the Winterbourne.

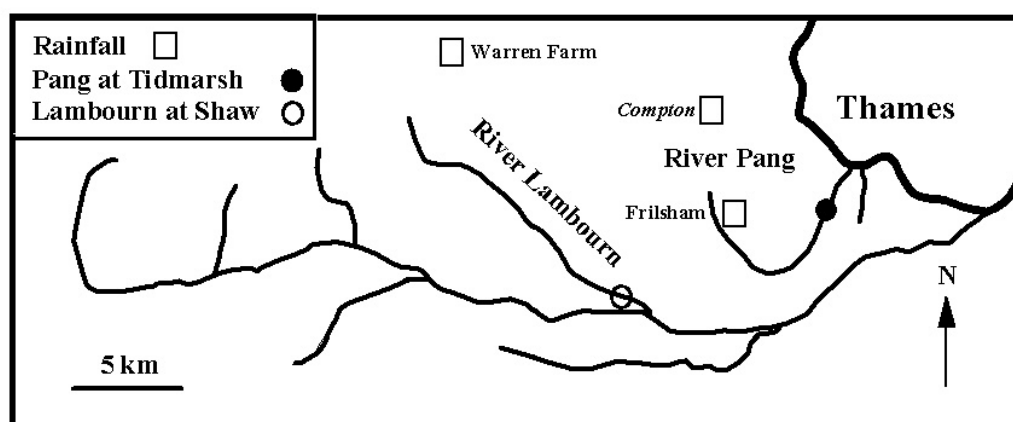


Fig. 1. Location map. The rainfall sites monitored in this study are at Warren Farm and at Frilsham. Rainfall was also monitored at Compton which links to information with the UK National Air Quality Archive, maintained by NETCEN, part of AEA Technology Environment, on behalf of the UK Department for Environment, Food & Rural Affairs and the Devolved Administrations. The Compton site is shown in italics to denote the difference from the other two rainfall sites.

## LOCATION

This paper deals with a rainfall and a river monitoring point on each of the Pang and the Lambourn catchments (Fig. 1). While several river monitoring points have been established (Neal *et al.*, 2000a; 2004) it is only data from the downstream sites of the Pang at Tidmarsh and the Lambourn at Shaw that are used here.

Within the Pang/Lambourn component of the LOCAR study, stream water quality monitoring began in April 2002, while rainfall water quality was measured when suitable sites were found in August 2002. For rainfall, the two rainfall collectors were of an open type and made of plastic: the funnel size was 300 mm diameter and small meshes were incorporated into the funnels to avoid contamination by wind-blown detritus and insects. One of the rainfall gauges is located mid-way down the Pang catchment at Frilsham Meadow and is at relatively low altitude (85 m a.s.l.). The other rainfall site is located near the top of the Lambourn catchment (200 m a.s.l.) by Warren Farm. Diffusion tube samplers for  $\text{NO}_2$  and  $\text{NH}_3$  were also located at these sites.

For the streams, the catchment and monitoring details are as follows:

### *Pang*

During the 'pre-LOCAR phase' of the study, only the lower River Pang at Tidmarsh was studied (Neal *et al.*, 2000a, 2004). Here, the Pang is within 3 km of Pangbourne and its confluence with the Thames. At Tidmarsh, the catchment has an area of about 150 km<sup>2</sup>. Monitoring began in August 1997 and is still continuing (now within the LOCAR programme).

### *Lambourn*

This study deals with a site at Shaw within 2 km of its confluence with the Kennet, in the market town of Newbury. Here the catchment area is about 234 km<sup>2</sup>.

## SAMPLING AND ANALYSIS

Rainfall samples were collected as weekly-integrated samples in 10 litre low density polyethylene (LDPE) containers. These samples were returned to the laboratories for filtering and chemical analysis. Stream water samples were collected weekly by 'grab sampling' and the waters were filtered in the field using 0.45µm filter circles (Whatman 47 mm diameter cellulose nitrate membranes). Prior to analysis, the samples were stored in glass and LDPE bottles with or without preservative depending upon specific requirements.

The details of storage and analytical methodologies were as follows:

### *pH and gran alkalinity*

pH was determined by a manual method on unfiltered samples stored in 50 ml leached glass bottles filled to the top to ensure minimum degassing of carbon dioxide (which affects pH) using a Radiometer GK2401C electrode and PHM 82 pH meter. The system was calibrated using reference pH 4 and 7 buffers and cross-checked against a 10<sup>-4</sup> N and 10<sup>-3</sup> N sulphuric acid standard. pH was recorded to the nearest 0.01. Gran alkalinity was determined electrometrically by a manual method on unfiltered samples stored in 500 ml acid washed LDPE bottles for stream waters and in 150 ml glass bottles for rain waters using a Radiometer GK2401C electrode and PHM 82 pH meter and a two-point acidimetric titration (pH 4 and 3). The titrant acid was 0.5N H<sub>2</sub>SO<sub>4</sub> for stream water samples, 0.05N H<sub>2</sub>SO<sub>4</sub> for rainwater samples. Gran alkalinity was recorded to the nearest µEq l<sup>-1</sup>. Electrical conductivity was determined by a manual method on unfiltered samples stored in 50 ml glass bottles using a Portland Electronics Model P335 meter with values recorded to the nearest 1 µS cm<sup>-1</sup>.

### *Major cation and trace element concentrations (Na, K, Ca, Mg, Li, Sr, Ba, Mn, Co, Fe, Zn, Cr, Ni, Al and Pb)*

These were determined by Inductively Coupled Plasma Optical Emission Spectroscopy using a Perkin-Elmer Optima 3300DV on filtered samples stored in 60 ml acid washed LDPE bottles. The samples were preserved with concentrated Aristar HNO<sub>3</sub> to 1% vv. Lowest quotable values for the major ions were Na, Mg – 0.1 mg l<sup>-1</sup>, Ca, K – 0.05 mg l<sup>-1</sup>, while for the trace elements the detection limits depended on the sensitivity of the method. Li, Sr, Ba, Mn, Co – 0.001 mg l<sup>-1</sup>, Fe, Zn, Cr, Ni – 0.003 mg l<sup>-1</sup>, Al, Pb – 0.01 mg l<sup>-1</sup>.

### *Major anions (NO<sub>3</sub>, NO<sub>2</sub>, SO<sub>4</sub>, Cl and F)*

These were determined by Ion Chromatography using a Dionex DX 500 system on filtered samples stored in 60 ml LDPE bottles. Lowest quotable values were Cl, NO<sub>3</sub> and SO<sub>4</sub> – 1 mg l<sup>-1</sup> (as species), NO<sub>2</sub> – 0.1 mg-NO<sub>2</sub> l<sup>-1</sup>, F – 0.05 mg l<sup>-1</sup>.

### *Ammonium*

This was determined by automated colourimetry based on the indophenol blue method (APHA-AWWA-WPCF, 1980). The samples were stored in 60 ml LDPE bottles prior to analysis. The lowest quotable value was 0.004 mg-NH<sub>4</sub> l<sup>-1</sup>.

### *Silicon*

This was determined by automated colourimetry based on the method of Truesdale and Smith (1976). The samples were stored in 60 ml LDPE bottles prior to analysis. The

lowest quotable value was 0.1 mg-Si l<sup>-1</sup>.

#### *Suspended sediments (SS)*

SS was determined by filtering 1 litre of sample onto a dried, weighed Whatman 47 mm diameter GF/C filter paper. The filter papers were then dried in an oven, overnight, at 80 °C and reweighed on a four-figure balance. The suspended sediment was calculated by difference and the results recorded to the nearest 0.1 mg l<sup>-1</sup>.

#### *Phosphorus speciation*

For phosphorus, three determinations were made: soluble reactive phosphorus (SRP), a measure of inorganic monomeric P; total dissolved P (TDP), a measure of the inorganic monomeric P, polymeric P and organic P; total P (TP), a measure of all the dissolved forms of P plus particulate P. From this, the dissolved hydrolysable P (DHP), which comprises polymeric P and organic P, was determined as the difference between TDP and SRP, and the particulate P (PP) was determined by the difference between TP and TDP. The terms SRP, DHP and PP are used in the remaining text to denote these three forms. SRP and TDP were determined on filtered samples, while TP was determined on an unfiltered sample. Separate samples were stored in 60 ml LDPE bottles. An automated colourimetric method was employed for SRP based on the method of Murphy and Riley 1962 (see also Neal *et al.* 2000b). The SRP analysis was undertaken on the day of sampling to avoid degradation of samples. TDP and TP were determined manually using the method of Eisenreich *et al.* (1975). The samples were analysed within 3 days of sampling. Within the TDP and TP methodologies, potassium persulphate and 1N H<sub>2</sub>SO<sub>4</sub> were added to the samples prior to autoclaving. The potassium persulphate was added to the samples in the field as a preservative. The lowest quotable value was 7 µg-P l<sup>-1</sup> for SRP, TDP and TP.

#### *Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN)*

These were determined by thermal oxidation using an Analytical Sciences Carbon/Nitrogen Analyser. The lowest quotable values were DOC – 0.1 mg-C l<sup>-1</sup> C and TN – 0.05 mg l<sup>-1</sup> N.

#### *Chlorophyll-a*

This was determined by extraction of sediment in a water sample (collected by GFC filtration) into ethanol and then a spectrophotometric measurement using a Pye Unicam SP1800 instrument (Marker, 1994). The results were recorded to the nearest 0.01 µg l<sup>-1</sup>.

For the determination of major cations and trace metals,

commercially available standards (Fisher Chemicals and BDH Spectrosol) were used for calibration. A quality control sample was run with each batch of samples immediately following the calibration and at the end of the run. Standards were also included every 10 samples to monitor for any drift. For the other analyses (major anions, NH<sub>4</sub>, Si, SRP, TDP, TP, DOC and TN) the standard solutions were prepared 'in-house'. A quality control sample was run with each batch of samples immediately following the calibration and standards were also included every 10 samples to monitor for any drift. The Wallingford laboratories participate in AQUACHECK which is a UKAS accredited proficiency testing scheme, an inter-laboratory testing scheme run by the UK Acid Waters Monitoring Network and an inter-laboratory testing scheme run by the Norwegian Institute for Water Research.

Passive diffusion tubes were used for the gas analysis (Atkins *et al.*, 1986; Sutton *et al.*, 2001). These tubes were changed every four weeks, and sent to an accredited commercial laboratory for analysis. The protocol for the NO<sub>2</sub> tubes was that used for the UK National Network (Bush *et al.*, 2000), that for the ammonia tubes was based on information in Sutton *et al.* (2001).

#### OTHER RAINFALL DATA

Within this study, data for a third rainfall site are presented. This is for a site in the north of the Pang catchment near the village of Compton (Fig 1). These data come from the UK National Air Quality Archive, maintained by part of AEA Technology Environment, on behalf of the UK Department for Environment, Food & Rural Affairs and the Devolved Administrations (NETCEN): the data were kindly supplied by Helen Lawrence. These data are included as they (a) provide a longer term record than that collected under LOCAR (i.e. March 1986 up to December 2002), (b) extend the spatial coverage and (c) the site is of intermediate altitude (105 m a.s.l.) between the near top and near bottom of catchment sites. Information on the Compton and other sites within the UK National Air Quality Archive is described by Vincent *et al.* (1996) and at their web site (<http://www.aeat.co.uk/netcen/airqual/networks/cdadidnk.html>).

#### THE ACCURACY AND MEANING OF INPUT-OUTPUT RELATIONSHIPS: STRATEGY AND IMPLEMENTATION

Within this paper, relations between rainfall input and river outputs are presented for water quality. Such information can be presented only as a first assessment because of several factors.

- There is a lack of long-term data for rainfall inputs and riverine outputs.
- There is a lack of certainty over the regional groundwater routing and the catchment, given that it is permeable and is therefore not 'water tight'. Thus, there is uncertainty over the water balance (Bradford, 2002).
- The river waters drain a Chalk aquifer with residence times of the order of decades. Thus, there is no direct correspondence between the rainfall inputs measured over a particular time period, and runoff collected over the same period — the latter represents a much longer time frame.

The primary focus is to examine the data collected during the LOCAR study and compared with (a) the UK National Air Quality Archive data and (b) the longer term data record for the Pang. Clearly there are issues of comparing 'like with like' given the different monitoring periods. Initial statistical and visual time-series analysis of the concentration data revealed that for many of the water quality determinands there is no clear trend in either the rainfall or the runoff chemistry (since 1986 in the case of rainfall and since 1997 in the case of the River Pang); for simplicity, the data summaries presented here cover the full monitoring periods rather than being restricted to the period of monitoring within LOCAR.

With regard to input-output fluxes, here only inputs from the atmosphere and outputs from the river are dealt with. No direct consideration is given to issues such as the amount of fertiliser input, the uptake of chemicals by the crops, the export of harvested crops and farm animals, etc. This additional information is not available here. Within the LOCAR programme, such analysis will be undertaken within the framework, for example, of the INCA and export coefficient approaches (Johnes, 1996; Whitehead *et al.*, 2002).

## Results

### RAINFALL

#### *General rainfall quality*

The rainfall at both Warren Farm and Frilsham Meadow is variable (Table 1). On occasion, the rainfall can be acidic, with pH as low as 4.2 and Gran alkalinities as low as  $-83 \mu\text{Eq l}^{-1}$ . However, on average, Gran alkalinities are positive, with maximum values as high as  $652 \mu\text{Eq l}^{-1}$ . The rainfall is often of 'dilute' chemistry, the major cations being Na and Ca, while the major anions are Cl and  $\text{SO}_4$ . The rainfall also contains measurable amounts of several trace metals, Al,

Fe, Mn and Zn in particular, and on rare occasions the concentrations can be particularly high: over  $200 \mu\text{g l}^{-1}$  for Al, Fe and Mn, and as high as  $2351 \mu\text{g l}^{-1}$  for Zn. In the case of Zn, the top six concentrations were for Warren Farm (concentrations  $> 200 \mu\text{g l}^{-1}$ ) and of these, three had concentrations  $>900 \mu\text{g l}^{-1}$ : thus the high concentrations cannot simply be considered as very occasional outlier points. In most cases, concentrations increase with decreasing volume of catch and this reflects (a) removal of particles in the atmosphere by rain and (b) dry deposition of particulate matter which accumulates on the rainfall collector each week. Factor analysis (with the occasional outlier values removed for the trace metals) reveals two main groupings for both Frilsham Meadow and Warren Farm and an extra group for Warren Farm:

- The first group describes about 35 and 45% of the total variance for Frilsham Meadow and Warren Farm, respectively. It comprises electrical conductivity (EC), SRP, DHP, PP,  $\text{NH}_4$ , F,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{SO}_4$ , total dissolved nitrogen (TDN), organic nitrogen, Si, K, Ca, B, Sr, Ba, Zn, Cu, Cr and Al. This group also includes a negative relationship with volume of catch. Many of these components are probably derived in significant part from local sources.
- The second group accounts for about 16 and 10% of the variance for Frilsham Meadow and Warren Farm, respectively. It comprises Na, Cl and Mg. This group corresponds to atmospheric inputs of 'sea salts'. For this group, there is an extremely strong linear correlation with intercepts not statistically significant from zero ( $p < 0.001$ ) as would be expected given the low lithogenic sources. These regressions are (in  $\text{mg l}^{-1}$  units: the  $\pm$  tem refers to two standard deviations):
  - $\text{Na} = 0.566 \pm 0.012 * \text{Cl} + 0.04 \pm 0.39$ :  $r^2 = 0.994$ ,  $N=36$ .
  - $\text{Mg} = 0.0685 \pm 0.0082 * \text{Cl} + 0.06 \pm 0.22$ :  $r^2 = 0.891$ ,  $N=36$ .
- In addition to the above two groupings, there is a strong third grouping for Warren Farm which accounts for about 15% of the variance. This grouping comprises Li, Mn, Co and Ni in negative relation with most of the first group; it is weakly linked to volume of catch. These inputs will be associated with local pollutant sources.

In terms of the relative input of the sea salts, the main chemical determinands involved are Na, Cl, K, Mg, B and Sr. To examine the relative input of 'non sea salt components', a comparison is made between ratios of the components to chloride for the rainfall ( $R_{\text{rain}}$ ) and for seawater ( $R_{\text{sw}}$ ) ( $R_{\text{rain:sw}}$ ; Table 2). This analysis reveals four categories.

Table 1. Rainfall statistics for Warren Farm and Frilsham Meadow.

		Average	FRILSHAM			Average	WARREN FARM		
			Average Catch weighted	Min.	Max.		Average Catch weighted	Min.	Max.
EC	$\mu\text{Scm}^{-1}$	34.1	24.3	11.0	121	62.9	40.4	16.0	150.0
pH		5.75	5.64	4.20	6.68	6.50	6.26	4.94	7.32
ALK	$\mu\text{Eq l}^{-1}$	4	-1	-83	124	107	55	-53	652
Na	$\text{mg l}^{-1}$	2.67	1.62	0.20	15.6	5.03	2.25	0.32	19.1
K	$\text{mg l}^{-1}$	0.28	0.13	0.04	0.99	0.53	0.23	0.06	2.44
Ca	$\text{mg l}^{-1}$	2.31	0.72	0.14	12.7	4.27	2.07	0.39	29.7
Mg	$\text{mg l}^{-1}$	0.39	0.22	0.06	1.91	0.74	0.33	0.08	2.30
Cl	$\text{mg l}^{-1}$	6.42	2.89	0.00	35.00	9.43	3.87	0.00	65.0
SO <sub>4</sub>	$\text{mg l}^{-1}$	6.55	2.05	0.00	72.5	10.0	3.03	0.00	112.5
F	$\text{mg l}^{-1}$	0.06	0.01	0.00	1.05	0.07	0.01	0.00	0.80
NO <sub>3</sub>	$\text{mg l}^{-1}\text{N}$	2.11	0.39	0.00	42.9	2.28	0.61	0.00	16.4
NO <sub>2</sub>	$\text{mg l}^{-1}\text{N}$	0.04	0.00	0.00	0.67	0.05	0.01	0.00	0.61
NH <sub>4</sub>	$\text{mg l}^{-1}\text{N}$	1.53	0.49	0.04	13.7	1.98	0.83	0.26	9.33
TDN	$\text{mg l}^{-1}\text{N}$	4.94	1.12	0.40	85.0	5.88	1.96	0.40	35.7
InorgN	$\text{mg l}^{-1}\text{N}$	3.68	0.88	0.04	57.26	4.31	1.45	0.26	26.31
Org N	$\text{mg l}^{-1}\text{N}$	1.26	0.24	0.36	27.74	1.57	0.51	0.14	9.39
SRP	$\mu\text{g l}^{-1}\text{P}$	68.4	10.7	0.0	1794	139.5	56.1	0.0	1126
DHP	$\mu\text{g l}^{-1}\text{P}$	20.5	4.3	0.0	346	54.5	11.7	0.0	883
PP	$\mu\text{g l}^{-1}\text{P}$	36.8	11.9	0.0	220	79.8	30.1	0.0	1268
DOC	$\text{mg l}^{-1}\text{C}$	3.87	1.63	0.30	19.50	5.01	2.00	0.50	24.00
Si	$\text{mg}^{-1}\text{Si}$	0.02	0.00	0.00	0.30	0.03	0.01	0.00	0.30
Al	$\mu\text{g l}^{-1}$	11.8	7.8	0.0	87.7	20.2	8.9	0.0	224
B	$\mu\text{g l}^{-1}$	2.8	1.2	0.0	12.1		3.7	1.5	0.0
20.7									
Ba	$\mu\text{g l}^{-1}$	4.2	2.1	0.4	12.0	3.8	2.3	0.6	15.1
Co	$\mu\text{g l}^{-1}$	0.2	0.2	0.0	0.8	2.9	0.9	0.0	116
Cr	$\mu\text{g l}^{-1}$	0.3	0.2	0.0	0.8	1.8	0.7	0.0	59.9
Cu	$\mu\text{g l}^{-1}$	2.6	0.9	0.0	10.9	2.3	0.7	0.0	13.0
Fe	$\mu\text{g l}^{-1}$	13.4	10.4	2.6	99	24.6	11.9	1.6	500
Li	$\mu\text{g l}^{-1}$	1.7	1.6	0.0	7.1	1.2	1.1	0.0	5.8
Mn	$\mu\text{g l}^{-1}$	15.5	6.7	1.0	109	11.8	6.6	1.1	124
Mo	$\mu\text{g l}^{-1}$	2.1	1.9	0.0	14.0	2.6	2.3	0.0	14.3
Ni	$\mu\text{g l}^{-1}$	2.7	2.0	0.0	23.2	5.4	2.3	0.0	38.8
Pb	$\mu\text{g l}^{-1}$	1.2	1.39	0.00	4.83	1.2	1.0	0.0	11.0
Sr	$\mu\text{g l}^{-1}$	6.5	2.6	0.5	34.0	9.9	4.9	1.1	50.4
Zn	$\mu\text{g l}^{-1}$	42.2	36.1	7.1	131	204	141	3.5	2351

Table 2. Element ratios to chloride for rainfall ( $R_{rain}$ ), including a comparison with sea water ratios ( $R_{rain:SW}$ ). The ratios for sea water are provided by data in Drever (2002). Rainfall data refer to catch-weighted averages (analysis for straight-averages gives very similar results).

		SEA WATER $R_{SW}$	FRILSHAM MEADOW $R_{rain}$	$R_{rain:SW}$	WARREN FARM $R_{rain}$	$R_{rain:SW}$
Na/Cl	mg:mg	0.556	0.561	1.01	0.561	1.01
K/Cl	mg:mg	0.021	0.042	2.05	0.059	2.81
Ca/Cl	mg:mg	0.021	0.365	17.2	0.512	24.0
Mg/Cl	mg:mg	0.067	0.058	0.87	0.084	1.26
SO <sub>4</sub> /Cl	Mg-SO <sub>4</sub> :mg	0.140	1.190	8.50	1.183	8.45
B/Cl	µg:mg	0.233	0.440	1.89	0.228	0.98
Sr/Cl	µg:mg	0.413	1.022	2.47	0.750	1.81

1. There are components where  $R_{rain:SW}$  is close to unity. These components are the main 'sea salts' Na, Cl and Mg.
2. There are components with  $R_{rain:SW}$  about two to four times that for seawater. These components are K, B and Sr and they have approximately an equal mix of marine and non-marine sources.
3. There is a group comprising Ca and SO<sub>4</sub> where clearly there are major non-marine sources ( $R_{rain:SW}$  8 to 24).
4. For the other determinands, the trace metals in particular, the non-marine inputs dominate ( $R_{rain:SW} > 30$ ).

#### WARREN FARM – FRILSHAM MEADOW COMPARISONS

The concentrations of the major elements are linearly correlated for most water quality determinands between the two sites. Linear correlation analysis (excluding occasional outlier values) indicates highly significant correlations ( $p < 0.002$ ) for the sea salts (Na, Cl and Mg), electrical conductivity, Gran alkalinity, B, Co, Cu, Cr, Ba, Ca, Cl, F, K, Pb, pH, Mn, Mo, Ni, NH<sub>4</sub>, NO<sub>3</sub>, TN, DHP, PP, Si, Sr, SO<sub>4</sub>, and Zn. Poorer correlations occur for Al, Li, Fe, NO<sub>2</sub>, SRP, DHP and PP. The concentrations for most chemical determinands are higher for Warren Farm compared with Frilsham Meadow (Table 3) and on average the enrichment is of the order of a factor of two. The enrichment factors are greatest for SRP and Cr (enrichment factors of 4 to 9), followed by Zn, Cu, Ca, DHP and PP (enrichment factors of 2 to 4) and then by Na, Cl, B, Sr, K, NH<sub>4</sub>, NO<sub>3</sub>, Mg and SO<sub>4</sub> (enrichment factors of 1.2 to 2).

With regard to the rainfall at the two sites, the volumes of catch, in ml, are highly correlated:

$$\text{Rainfall}_{\text{Frilsham}} = 0.88 \pm 0.06 * \text{Rainfall}_{\text{Warren Farm}} + 56 \pm 615$$

$$N = 46, R^2 = 0.952.$$

On average, the rainfall catch at Frilsham is about 8% lower than that at Warren Farm; this compares well with long term averages of rainfall for the two catchments (IH, 1998) where the Pang catchment has an estimated rainfall input about 5% lower than that of the Lambourn.

The concentrations of many determinands are inversely related to the volume of catch at each site and there is bound to be some correlation of concentrations and indeed of fluxes as volumes are strongly correlated. N.B. here correlation expressions are used, not regression calculations — regression assumes a dependent and an independent variable, which is not the case with this dataset.

In terms of chemical flux, then the higher concentrations at Warren farm coupled with a (slightly) higher volume of catch than Frilsham, indicates a higher flux term for the Lambourn for many determinands.

#### WARREN FARM – FRILSHAM MEADOW - COMPTON COMPARISONS

There is also a systematic difference between the water quality of the Compton site and that of Frilsham Meadow and Compton site has water quality nearer to that for Warren Farm (Table 3). Taking the average volume of catch weighted concentration for each determinand across the three sites and comparing values with those for each site and each determinand shows that:

- Frilsham Meadow has average concentrations for the various determinands between 0.14 and 0.8 times that for the area-average (average 0.6).
- Warren Farm and Compton have average concentrations for the various determinands between 0.84 and 1.64 times that for the average across the sites (average 1.11 and 1.29, respectively).
- There are some marked differences for some



Table 3. A comparison of volume weighted water quality averages for rainfall at Frilsham, Warren Farm and Compton. The “average all” column refers to the mean volume weighted concentration for each determinand at Frilsham, Warren Farm and Compton. The ratio of averages is the ratio of the average volume-weighted concentration at a particular site divided by the average for all three sites. The units are all in mg l<sup>-1</sup> except for soluble reactive phosphorus which has units of µg l<sup>-1</sup> P.

	Average	Average			Ratio of averages		
	All	Frilsham	Warren Farm	Compton	Frilsham	Warren Farm	Compton
Na	2.01	1.62	2.25	2.17	0.80	1.12	1.08
K	0.27	0.13	0.23	0.44	0.48	0.88	1.64
Ca	1.29	0.72	2.07	1.08	0.56	1.60	0.84
Mg	0.30	0.22	0.33	0.34	0.75	1.11	1.14
NH <sub>4</sub> -N	0.94	0.49	0.83	1.51	0.52	0.88	1.60
NO <sub>3</sub> -N	0.55	0.39	0.61	0.66	0.70	1.11	1.19
Cl	3.61	2.89	3.87	4.06	0.80	1.07	1.13
SO <sub>4</sub>	3.14	2.05	3.03	4.32	0.65	0.97	1.38
SRP	46.1	10.7	56.1	71.6	0.23	1.22	1.65
Avg					0.60	1.11	1.29
Min					0.14	0.88	0.84
Max					0.80	1.60	1.64

determinands for the Warren Farm and Compton sites.

In particular, enrichments are higher at Warren Farm for Ca and enrichments are higher at Compton for K, NH<sub>4</sub>, SO<sub>4</sub> and SRP. These enrichments are up to a factor of about 2.

#### RIVER WATER CHEMISTRY

The river water quality corresponds to that typical for Chalk fed aquifers (Owen *et al.*, 1991) except that the stream waters have higher pHs due to degassing of carbon dioxide (Neal *et al.*, 2002b). Thus, the waters are calcium- and bicarbonate bearing and have relatively uniform concentrations. Agricultural inputs may well result in enhanced levels of nutrients, nitrate, SRP and PP in particular but other factors come into play (Neal *et al.*, 2004). For nitrate, the concentrations are higher during the winter months due to a combination of increased surface runoff with higher NO<sub>3</sub> sources from fertilisers, and less biological uptake. Point source inputs (sewage treatment works effluent) result in enhanced concentrations of several major ions as well as B. A detailed description of the water quality of the Pang and Lambourn can be found in Neal *et al.* (2000a, 2004). In general, the Pang and the Lambourn have very similar water quality, with only relatively minor variations in average and ranges in chemistry (Table 4): the differences in chemistry are discussed by Neal *et al.* (2004).

#### RAINFALL – RUNOFF RELATIONSHIPS

Because of the variation in rainfall chemistry across the Pang and Lambourn, it is not possible to obtain a truly accurate measurement of the wet deposition input of chemicals to either of the catchments. For the present purposes, the fluxes are calculated using the Frilsham Meadow and Warren Farm as measures of the wet input from the Pang and Lambourn, respectively. For the streams, the flow weighted average concentrations were used. For the estimation of wet-input output relationships, the flow weighted concentrations were multiplied by the long term averages for rainfall and river flow for the two catchments. These long term averages are taken from the Hydrological data for the UK (IH, 1998): for the Pang, rainfall 702mm, runoff 162 mm; for the Lambourn, rainfall 739 mm, runoff 231 mm. The results of this exercise are shown in Table 5. There are very wide ranges of atmospheric input– riverine output relationships. Clearly the catchment balances will be influenced by the size of the flux involved as for example the net riverine output–atmospheric input fluxes will often be smaller for the trace elements compared to the majors. An estimate of source in runoff from the catchment is taken as the ratio of the net flux to the river flux, expressed as a percentage (%<sub>c</sub> = 100\*(riverine output–atmospheric input)/riverine output), but large negative values can occur when the atmospheric input flux is particularly high. The relationships are very similar for both the catchments and the salient details are as follows.

- A net riverine export relative to the atmospheric input

Table 4. Pang and Lambourn water quality statistics

		PANG: TIDMARSH				LAMBOURN: SHAW			
		<i>Avg</i>	<i>Avgfw</i>	<i>Min</i>	<i>Max</i>	<i>Avg</i>	<i>Avgfw</i>	<i>Min</i>	<i>Max</i>
EC	$\mu\text{Scm}^{-1}$	618	627	460	674	593	596	554	627
pH		7.91	7.87	7.57	8.18	7.91	7.90	7.47	8.15
ALK	$\mu\text{Eq/l}$	4732	4786	2752	5265	4702	4681	4249	4947
Na	$\text{mg l}^{-1}$	11.1	11.5	9.4	13.7	9.20	9.29	8.53	10.87
K	$\text{mg l}^{-1}$	3.01	3.00	1.92	6.99	1.86	1.85	1.38	4.70
Ca	$\text{mg l}^{-1}$	108.7	109.9	69.3	119.0	109.0	109.0	92.0	113.2
Mg	$\text{mg l}^{-1}$	3.05	3.01	2.1	4.57	1.77	1.77	1.66	1.85
Cl	$\text{mg l}^{-1}$	22.5	23.0	18.0	26.5	18.1	18.6	15.0	22.5
SO <sub>4</sub>	$\text{mg l}^{-1}$	20.0	20.0	16.0	32.0	13.9	14.8	12.0	18.5
F	$\text{mg l}^{-1}$	0.17	0.19	0.12	0.24	0.14	0.14	0.11	0.19
NO <sub>3</sub>	$\text{mg l}^{-1}\text{N}$	7.09	7.58	4.52	8.92	6.94	7.27	5.42	8.58
NO <sub>2</sub>	$\text{mg l}^{-1}\text{N}$	0.06	0.07	0.00	0.15	0.04	0.04	0.00	0.15
NH <sub>4</sub>	$\text{mg l}^{-1}\text{N}$	0.03	0.04	0.00	0.08	0.05	0.04	0.01	0.14
TN	$\text{mg l}^{-1}\text{N}$	7.88	8.36	6.20	10.30	7.64	7.92	6.70	9.50
Inorg N	$\text{mg l}^{-1}\text{N}$	7.19	7.69	4.52	9.15	7.03	7.35	5.43	8.88
Org N	$\text{mg l}^{-1}\text{N}$	0.69	0.67	1.68	1.15	0.62	0.57	1.27	0.62
SRP	$\mu\text{g l}^{-1}\text{P}$	47	57	7	134	97	94	55	228
DHP	$\mu\text{g l}^{-1}\text{P}$	13	14	0	15	15	14	17	5
PP	$\mu\text{g l}^{-1}\text{P}$	17	19	0	128	14	14	13	36
DOC	$\text{mg l}^{-1}\text{C}$	2.10	2.27	0.80	8.30	1.54	1.48	0.70	6.20
Si	$\text{mg l}^{-1}\text{Si}$	6.92	6.84	4.60	8.00	6.91	6.82	5.90	7.50
Al	$\mu\text{g l}^{-1}$	10.0	13.3	0.0	165.9	9.4	10.3	0.0	40.0
B	$\mu\text{g l}^{-1}$	21.0	21.4	10.0	35.1	18.9	19.0	14.8	23.4
Ba	$\mu\text{g l}^{-1}$	28.8	28.8	21.0	32.6	19.4	18.8	16.2	24.4
Co	$\mu\text{g l}^{-1}$	0.2	0.2	0.0	1.1	0.2	0.2	0.0	1.5
Cr	$\mu\text{g l}^{-1}$	0.2	0.1	0.0	0.7	0.1	0.1	0.0	0.6
Fe	$\mu\text{g l}^{-1}$	20.4	25.3	4.0	197.1	10.2	9.3	3.7	30.6
Mn	$\mu\text{g l}^{-1}$	3.3	4.1	1.0	8.5	3.1	3.0	1.7	7.0
Ni	$\mu\text{g l}^{-1}$	2.8	3.1	0.0	4.4	2.1	2.2	0.0	4.4
Sr	$\mu\text{g l}^{-1}$	309	300	192	352	257	255	207	278
Zn	$\mu\text{g l}^{-1}$	23.9	28.2	0.0	129.2	16.2	17.6	0.2	41.1

with predominantly catchment sources. These are the major weathering products from the catchment: Ca, Sr, Alkalinity (bicarbonate) from calcite dissolution and Si from silicate breakdown.

- A net riverine export relative to the atmospheric input with significant within catchment sources. These include weathering products (Mg, Ba, F), components associated with agricultural practices (Ba, NO<sub>2</sub>) including fertilizer application (NO<sub>2</sub>, NO<sub>3</sub>, K, total N) and point source inputs (B).
- A net riverine export relative to the atmospheric input with significant atmospheric inputs. This group comprises Na, Cl, inorganic/total N, and SO<sub>4</sub>.
- A net retention of the atmospheric inputs relative to the riverine outputs. These comprise components with a highly significant atmospheric input with loss to the

Table 5. Pang and Lambourn wet-deposition-input output relationships. All concentrations in elemental terms except sulphate and alkalinity.

		PANG				LAMBOURN			
		Rain	River	Net flux	% catch. source	Rain	River	Netflux	% catch. source
Alk	eq ha <sup>-1</sup> yr <sup>-1</sup>	-9	5456	5466	100	406	10811	10405	96
Na	kg ha <sup>-1</sup> yr <sup>-1</sup>	11.34	13.05	1.71	13	14.29	21.46	7.17	33
K	kg ha <sup>-1</sup> yr <sup>-1</sup>	0.89	3.42	2.54	74	1.33	4.27	2.94	69
Ca	kg ha <sup>-1</sup> yr <sup>-1</sup>	5.05	125.27	120.21	96	10.31	251.85	241.55	96
Mg	kg ha <sup>-1</sup> yr <sup>-1</sup>	1.57	3.43	1.87	54	2.03	4.09	2.05	50
Cl	kg ha <sup>-1</sup> yr <sup>-1</sup>	20.31	26.20	5.89	22	24.98	42.88	17.90	42
SO <sub>4</sub>	kg ha <sup>-1</sup> yr <sup>-1</sup>	14.40	22.74	8.35	37	18.79	34.14	15.36	45
F	kg ha <sup>-1</sup> yr <sup>-1</sup>	0.05	0.22	0.17	77	0.07	0.32	0.25	79
NO <sub>3</sub> -N	kg ha <sup>-1</sup> yr <sup>-1</sup>	2.71	8.65	5.93	69	3.69	16.78	13.09	78
NO <sub>2</sub> -N	kg ha <sup>-1</sup> yr <sup>-1</sup>	0.02	0.08	0.05	70	0.04	0.10	0.05	53
NH <sub>4</sub> -N	kg ha <sup>-1</sup> yr <sup>-1</sup>	3.42	0.04	-3.38	-8154	4.86	0.10	-4.76	-4832
TN	kg ha <sup>-1</sup> yr <sup>-1</sup>	7.86	9.53	1.67	18	11.36	18.30	6.93	38
Inorg N	kg ha <sup>-1</sup> yr <sup>-1</sup>	6.15	8.76	2.61	30	8.60	16.97	8.38	49
Org N	kg ha <sup>-1</sup> yr <sup>-1</sup>	1.70	0.76	-0.94	-123	2.76	1.32	-1.44	-109
SRP	g ha <sup>-1</sup> yr <sup>-1</sup>	74.97	65.44	-9.53	-15	231.04	216.38	-14.66	-7
DHP	g ha <sup>-1</sup> yr <sup>-1</sup>	30.13	15.93	-14.20	-47	48.18	31.96	-16.22	-51
PP	g ha <sup>-1</sup> yr <sup>-1</sup>	83.39	21.92	-61.46	-280	123.96	32.96	-91.00	-276
TP	g ha <sup>-1</sup> yr <sup>-1</sup>	188.49	103.29	-85.20	-82	403.18	281.30	-121.88	-433
DOC	kg ha <sup>-1</sup> yr <sup>-1</sup>	11.44	2.59	-8.85	-342	13.40	3.42	-9.98	-292
Si	kg ha <sup>-1</sup> yr <sup>-1</sup>	0.02	7.80	7.78	100	0.04	15.76	15.73	100
Al	g ha <sup>-1</sup> yr <sup>-1</sup>	54.71	15.20	-39.52	-260	61.68	18.51	-43.17	-233
B	g ha <sup>-1</sup> yr <sup>-1</sup>	8.57	24.36	15.79	65	10.04	43.81	33.77	77
Ba	g ha <sup>-1</sup> yr <sup>-1</sup>	14.77	32.85	18.08	55	16.27	43.44	27.17	63
Co	g ha <sup>-1</sup> yr <sup>-1</sup>	1.47	0.22	-1.25	-576	4.12	0.35	-3.77	-1075
Cr	g ha <sup>-1</sup> yr <sup>-1</sup>	1.70	0.13	-1.57	-1177	3.60	0.17	-3.43	-2044
Fe	g ha <sup>-1</sup> yr <sup>-1</sup>	73.01	28.81	-44.20	-153	82.27	21.46	-60.81	-283
Mn	g ha <sup>-1</sup> yr <sup>-1</sup>	47.02	4.63	-42.38	-915	49.12	6.89	-42.23	-613
Ni	g ha <sup>-1</sup> yr <sup>-1</sup>	13.85	3.50	-10.35	-296	15.79	5.07	-10.72	-211
Sr	g ha <sup>-1</sup> yr <sup>-1</sup>	17.92	342.41	324.49	95	27.57	587.92	560.34	95
Zn	g ha <sup>-1</sup> yr <sup>-1</sup>	253.81	32.14	-221.66	-690	654.19	40.63	-613.57	-1510

catchment either due to solubility controls (e.g. the trace metals which precipitate in the alkaline water encountered in the aquifer and the river) or to biological uptake and sorption onto sediments (e.g. SRP species and NH<sub>4</sub>). The relative extent of uptake broadly divides into four groups with increasing order Fe/SRP/Organic-N/ Al/Ni/DHP, Mn/PP, Co/Zn/Cr and NH<sub>4</sub>.

#### DRY DEPOSITION OF NITROGEN SPECIES

Table 6 shows a comparison of the dry and wet input fluxes for oxidised and reduced nitrogen. Dry deposition has been calculated by a deposition velocity approach, using 2 mm s<sup>-1</sup> for oxidised N and 10 mm s<sup>-1</sup> for reduced N (Smith *et al.*, 2000): similar estimates are found from regional modelling as estimated by CEH Edinburgh (for moorland in the Compton area grid, the deposition is 8.3 and 23.1 kg

Table 6. Estimated concentrations of NO<sub>2</sub> and NH<sub>3</sub> in rainfall and wet and dry deposition to the catchments

Site	Concentrations ( $\mu\text{g m}^{-3}$ )		Dry deposition ( $\text{kg N ha}^{-1} \text{yr}^{-1}$ )		Wet deposition ( $\text{kg N ha}^{-1} \text{yr}^{-1}$ )		Total deposition ( $\text{kg N ha}^{-1} \text{yr}^{-1}$ )	
	NO <sub>2</sub>	NH <sub>3</sub>	NO <sub>2</sub>	NH <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
Frilsham	20.0	21.8	3.8	21.8	2.7	3.4	6.5	25.2
Warren Farm	16.8	19.1	3.2	19.1	3.7	4.9	6.9	24.0

N ha<sup>-1</sup> yr<sup>-1</sup> for NO<sub>x</sub> and NH<sub>3</sub> respectively). The input of reduced nitrogen is dominated by the dry deposition component, whereas the wet and dry deposition of oxidised N is about equal. There may be other, non-measured dry deposition components, nitric acid vapour in particular. These input fluxes compare with inorganic N outputs of 8.8 and 17.0 kg N ha<sup>-1</sup> yr<sup>-1</sup> for the Pang and Lambourn respectively (Table 5) — in other words the catchments are apparently retaining on average 50% or more of the atmospheric N inputs. Given that there are N fertiliser inputs as well, there must either be a large terrestrial/riverine sink for nitrogen or it is being lost to groundwater from which it may eventually emerge after a time delay.

Dry deposition of ammonia especially is likely to be spatially very variable, and two sampling sites are not adequate to estimate deposition over such large areas. The deposition velocities used are appropriate for low vegetation — deposition to forests would be about three times greater for the same concentration of ammonia. Forests also increase the dry deposition of sulphur dioxide and particulates, and the extent of capture is very variable (Neal *et al.*, 1994; Robson *et al.*, 1994): estimates of non marine sulphate deposition by CEH Edinburgh for moorland in the Compton area grid is 24.5 kg SO<sub>4</sub> ha<sup>-1</sup> yr<sup>-1</sup>. Better site specific estimates of dry deposition to the catchment will require a combination of more measurements with modelling the response of deposition to spatial variation in the physical environment. Spatial variation in wet deposition is also important as mentioned above. Clearly a network of sites is required to determine both the wet and the dry deposition.

## Discussion

This study shows that the rainfall in this rural/agricultural area is not 'clean' as it contains both nutrient and trace element contaminants and the findings are enlightening in relation to issues of catchment hydrochemistry and catchment balances, and for management purposes in relation to the nutrients N and P.

For rainfall, the water quality is variable in relation to types of input (sea salts and pollutants), volume of catch and location. The atmospheric fluxes to the two catchments

studied are thus hard to pin down. Further, for NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, there are large gaseous deposition terms which are hard to quantify with current information. The same is probably true for SO<sub>4</sub> where perhaps a half of the input may come from dry deposition.

Input-output relationships show some expected relationships, which take three forms:

1. There is the dominance of the major weathering products from catchment sources (Ca, Sr and bicarbonate).
2. There are mixed sources of inputs linked with catchment sources tied in to (a) within-catchment weathering processes (Mg and Ba); (b) agricultural runoff (NO<sub>3</sub><sup>-</sup> and K); and (c) point sources (B, Na, and Cl).
3. There is the large removal of atmospheric inputs of trace transitional metals and NH<sub>4</sub><sup>+</sup>. In the case of the transition metals, they will be retained within the catchment because of the relatively high pH encountered within the catchment as solubility controls become operative. For NH<sub>4</sub><sup>+</sup> uptake by the vegetation and sediments will occur and there is also conversion to NO<sub>3</sub><sup>-</sup>.

However, what was not expected was that the catchments are apparently retaining phosphorus as SRP, DHP and PP and (if dry deposition is included) nitrogen. Rather, what might be expected would be a marked net export of these elements from the catchment to the river due to agricultural and sewage effluent on top of atmospheric inputs. Even ignoring the issues of N and P inputs from the atmosphere, with average riverine fluxes of about 0.2 kg-P ha<sup>-1</sup> yr<sup>-1</sup> and 9 kg-N ha<sup>-1</sup> yr<sup>-1</sup> for P and N respectively, the agricultural inputs seem to much larger, with typical values for farmland of 13 kg-P ha<sup>-1</sup> yr<sup>-1</sup> (Leinweber *et al.*, 2002) and 250 kg-N ha<sup>-1</sup> yr<sup>-1</sup> (Hatch *et al.*, 2002) for P and N, respectively. There are several alternatives, or some combination of these alternatives, to explain these features:

1. The catchments are strong sinks for NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and SRP. This is a distinct possibility as
  - a. They are essential nutrients for plant growth.
  - b. NH<sub>4</sub><sup>+</sup> and SRP are strongly sorbed to the soils: SRP is

also sorbed onto the riverine sediments.

- c. There is long-term aquifer storage (for the agricultural sources at least) and this will facilitate within-aquifer degradation and in the case of SRP, inclusion into calcite lattices.
2. Atmospheric inputs are overestimated or misjudged. This might well be the case in that the increasing concentrations with lower volumes of catch, coupled with the spatial variability in rainfall chemistry may mean that there are localised sources such as insect capture by the funnel. This is observed for Warren Farm where determinand concentrations are generally higher than at Frilsham Meadow. Insect inputs are probably particularly important for SRP, DHP and PP where normally none of these P species would be considered as a significant term: the presence of organic N (and also organic P as DHP) indicates such biological inputs. However, dust inputs (wind driven and also from movement of livestock) and general agricultural practices (e.g. fertiliser applications with associated aerosol sprays) may also be important as there are local farming activities going on near the monitoring sites. Whether or not some of these inputs should be considered as contamination or 'true' atmospheric inputs remains debatable. However, further consideration of this aspect is clearly needed and the agricultural input may well be dominant.
3. The riverine and groundwater exports are underestimated. For the river, the lack of detailed storm events may result in an underestimate of flux as it is at these times when agricultural sources of N and P might be expected. In the case of the groundwater there are issues of the hydrological closure of the catchments.
4. There are issues of residence storage times with inputs from both the atmosphere and from agriculture, aquifer storage and riverine discharges that have changed and are changing with time.
5. SRP can be removed from the groundwater areas by co-precipitation with calcite (Neal, 2001; Jarvie *et al.*, 2002a,b).
6. There are additional export terms for N and P. In particular, there is the issue of the export of harvested crops and farm animals (Hatch *et al.*, 2002; Leinweber *et al.*, 2002).

This work provides a starting point within the LOCAR programme in respect of water quality, giving an important backdrop for separating out atmospheric from within-catchment sources. This is important for example in trying to type groundwater inputs from different parts of the aquifer using base cation data in relation to near surface sources.

For example, the rainfall data provides 'endmember' chemistries for use in two/multi-component mixing studies such as End Member Mixing Analysis (EMMA: Christophersen *et al.*, 1990). Further, the B data provide important information for assessing human effluent sources as there are important issues of the significance of septic tank and sewage treatment work effluent inputs for SRP to the catchment/river. Such information is of particular importance for the management of riverine ecology as P is often the limiting nutrient. This links to the issues of whether agriculture or sewage provides the major source of SRP to the rivers at critical times of plant/algae growth.

This study highlights concerns over what is actually being collected and whether or not the rainfall flux estimates contain a significant term for 'catchment cycling' — in other words, the rainfall fluxes are derived partly from sources within the catchments and are thus not genuine inputs. Such concerns are particularly acute for nitrogen and phosphorus species. The concerns link to issues of insect and particulate matter redistributions of nutrients across catchments and/or between catchments and there is a need to consider more fully across-catchment insect and particulate nutrient vectors of flux. The study also underlines the potential importance of gaseous deposition for  $\text{SO}_4$ ,  $\text{NO}_3$  and  $\text{NH}_4$  from both local sources and sources further afield. Clearly, there are significant unknowns/uncertainties with regard to the net input output flux and a much wider flux inventory approach is required than the one given here. This issue is of importance to the environmental management for many lowland UK catchments with regard to the nutrients. More attention, therefore, needs to be given in future research in the environmental nutrients field of rural/agricultural sustainability to (a) assessing the significance of atmospheric sources, (b) the role of farming in the distribution of local inputs and outputs of nutrients within catchments and (c) the relative importance of treated sewage as direct inputs to the river and as indirect near-river supplies (e.g. from septic tanks and animal slurry storage).

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