Article (refereed) - postprint

Neal, Colin; Bowes, Michael; Jarvie, Helen P.; Scholefield, Paul; Leeks, Graham; Neal, Margaret; Rowland, Philip; Wickham, Heather; Harman, Sarah; Armstrong, Linda; Sleep, Darren; Lawlor, Alan; Davies, Cynthia E.. 2012 Lowland river water quality: a new UK data resource for process and environmental management analysis. *Hydrological Processes*, 26 (6). 949-960. 10.1002/hyp.8344

# Lowland river water quality: a new UK data resource for process and environmental management analysis

Colin Neal[1*], Michael Bowes[1a], Helen P. Jarvie[1], Paul Scholefield[2b], Graham Leeks[1c], Margaret Neal[1], Philip Rowland[2], Heather Wickham[1], Sarah Harman[1], Linda Armstrong[1], Darren Sleep[2], Alan Lawlor[2], Cynthia E Davies[1]
[1]Centre for Ecology and Hydrology, Crowmarsh Gifford, Wallingford, OXON, OX10 8BB, UK
[2]Centre for Ecology and Hydrology, Lancaster. Lancaster Environment Centre, Library Avenue, Bailrigg, Lancaster, LA1 4AP, UK.

Corresponding authors email: a, the Thames Basin mibo@ceh.ac.uk; b, the Ribble and Wyre; c, the LOIS rivers gjll@ceh.ac.uk: * Instigator, now retired.

## 1. Introduction

Increasing emphasis is being placed on characterising the water quality of agricultural and urban/industrially impacted river systems based on extensive, high quality monitoring associated with major research programmes (Neal et al., 2003; Billen et al., 2007). Such data complement long-standing environmental monitoring as part of the management of both riverine and lacustrine water bodies by regulatory agencies such as the Environment Agency of England and Wales, and the Scottish Environmental Protection Agency (Robson and Neal, 1997a,b; Jarvie et al., 2003a). Both types of data are vital for addressing issues such as sewage effluent and agricultural runoff of pollutants to water courses and their environmental consequences and making the information freely available for research and management purposes is of critical importance (Tromp-van Meerfield et al., 2008; Schofield et al., 2009). At international levels, increasing attention is placed upon basin scale management (Billen et al., 2007) particularly in the light of environmental policy contained within the Water Framework Directive of the European Commission (CEC, 1991, 2000, 2008; Neal and Jarvie, 2005). There are social and economic needs that require factoring into the management options for environmental solutions (Bateman et al., 2006). This occurs due to rising pressures of population increase and mobility, upon water resources, in addition to the impacts of changing climate, coupled with the current difficult economic environment for our peri-urban and urban centres (Rodda, 2007). It also impinges on other issues and challenges such as scarcer resources (e.g. fertilisers), carbon footprints and food security (Davies, 2011). For the UK, over 80% of the population live in urban areas, yet these areas cover only 10% of the land (Leeks et al., 2006). A critical point for UK river systems is that the issues are multifaceted (Neal, 2001). This is due to a relatively high population density and a landscape that is impacted by many factors over many time scales. Such factors include deforestation in Neolithic times, historic heavy metal contamination of flood plains from mining activity during Roman times and the land enclosures around the 16$^{th}$ century. They also include the major population and industrial change associated with the Industrial Revolution of the 18$^{th}$ and 19$^{th}$ century through to the current post-industrial society. Historically, the rivers provided water resource, power, transportation routes, and a rapid route of effluent disposal. This provides the template for studying contemporary population, industry and agricultural distribution and change (Neal, 2001).

Many of the environmental pressures on water resources and water quality are greatest within the UK lowlands which have the highest population density, industrialisation and agriculture. Three large scale integrated UK programmes funded by the Natural Environment Research Council (NERC) have provided key research on UK lowland rivers: the Land Ocean Interaction Study (LOIS; Leeks and Jarvie, 1998), the Urban Regeneration and the Environment programme (URGENT, Leeks et al., 2006) and the Lowland Catchment Research Programme (LOCAR, Wheater and Peach, 2004). For these community research programmes, the Centre of Ecology and Hydrology (CEH) within NERC has undertaken core monitoring across major eastern UK river basins. These basins span from the rural Tweed on the Scotland-England border to the Humber draining the industrial heartlands of northeastern England and to the agricultural areas of the Thames Basin in south-eastern England.

Here, an overview is provided of our findings from within these and other programmes and critical issues are raised linked to water storage and environmental management needs. Reference is also made to recent studies with the development of a source to sea initiative conducted in CEH for the Ribble and Wyre catchments that encompasses upland moorland to the industrial base of the north west of England (Neal et al., 2011a). Within CEH/NERC, major infrastructure investment is being made to develop a readily accessible data portal (the CEH Information Gateway: www.gateway.ceh.ac.uk) to make available the wealth of environmental information and data collected over several decades. Here the free availability of these data records to the wider research community through this portal is flagged to allow full exploitation of this resource. A copy of the data and supplementary information is provided here as a reference point, but copyright rests within CEH/NERC and the gateway provides the key link to licensing all of the data collected and data currently being collected. It provides data that is valuable for example in environmental impact modelling and source apportionment studies (Bowes et al., 2008; Wade et al., 2002, 2004; Whitehead et al., 1998) and the commentary is a foundation document for the database, a bibliography and the reference point for citations.

The paper provides as complete a record as possible at a time of retirement for the lead author as background knowledge will be lost. In this regard, the readership is also directed to a major data resource for the upland studies at Plynlimon in mid-Wales (Neal et al., 2011b).

## 2. Background

The data come from monitoring of one to several years duration for 5 eastern UK basins for rivers that drain to the North Sea or the English Channel as supplemented by the new data for the Ribble and Wyre (Table 1, Figure 1). They include data for the Kennet and Avon Canal and sewage treatment works (STWs) final effluent data across the Thames Basin. Each location was monitored on a weekly to monthly basis for at least one year and in many cases for several years between the early 1990s and the late 2000s (Table 1). A brief comment on each region is provided below with catchment areas in brackets. For the Tweed, Wear, Humber and Great Ouse basins, catchment statistical summaries of concentrations and flux inventories are provided by Neal and Robson (2000) and Neal and Davies (2003). Neal et al. (2011a) provide the corresponding information on concentrations for the Ribble and Wyre. Key research references are provided within each section.

**Tweed** (4400 km$^2$). The Tweed basin is located on the eastern side of the mainland UK, around the border between Scotland and England. The basin includes upland areas of moorland and rough pasture for hill farming (mainly sheep), and arable areas in the lowlands. The underlying geology is mainly greywacke, shale, mudstone and limestone. Reference: Neal et al., 1997b.
**Wear** (1044 km$^2$). The Wear basin, of northeastern England has acid moorland uplands and arable land and urban centres in the lowlands, with underlying geology of limestone, millstone grit, shale and mudstones. Reference: Neal et al., 2000d.
**Humber** (24000 km$^2$). The Humber Basin is a major drainage area for the eastern UK and it has several rivers and sub-basins. In the northern part of the basin, the main rivers (Swale, Ure, Nidd, Yorkshire Ouse, Derwent and Wharfe) drain moorland headwater areas and lowland agricultural land. In the southern Humber, the main rivers (Aire, Calder, Don and Trent) drain the industrial heartland of central and eastern England. Across the region, the underlying bedrock varies between sandstone, grit, clays and limestone. References: Neal et al., 1997a; Jarvie et al., 1997.
**Great Ouse** (8600 km$^2$). The Great Ouse drains central/south-eastern England and it flows through lowland agricultural areas and several market towns. The bedrock comprises clay and limestone (Chalk) sediments. Reference: Neal et al., 2000c.
**Thames** (12935 km$^2$). The Thames drains a large part of south-eastern England with major effluent inputs from large population centres (including London near its estuary). The underlying geology is dominated by high permeability chalk and Oolitic limestone and low permeability clay. The tributaries studied were Cherwell, Ray, and Thame that have basins of generally low permeability (Neal et al., 2006a,b, 2010a,b) and the Pang, Lambourn, Kennet and Dun that are mainly chalk aquifer sourced (Neal et al., 2002a, 2005a,b, 2006c, 2010a,b,c). In addition to the UK river studies, for the Kennet and Dun, Kennet and Avon Canal and its supply reservoir have also been studied as there are issues of eutrophication and in the case of the canal with its drainage to the River Dun, fish kills (Johnson et al., 1998; Neal et al., 2005a, 2006b, 2010c).
**Ribble and Wyre** (1084 and 273 km$^2$, respectively). Both rivers drain acid moorland uplands in the North West of England on passage to the Irish Sea. The lower Ribble basin includes urban/industrial areas while the Wyre basin is much more rural in nature. Reference: Neal et al., 2011a.

The data provided here as an electronic attachment, is uncensored as is needed for research purposes. Hence the data includes values below detection limits (in some cases negative). Details of analytical methodologies, detection limits, lowest quotable values as well as site locations are also presented electronically as supplementary material. Of the data, especial care is needed with regards to the total acid available components as the particulate component will not have fully leached.

Flow data cannot be provided here as they were collected by other organisations. However, flow data may be obtained from the National River flow Archive at http://www.ceh.ac.uk/data/nrfa/ (Marsh and Hannaford, 2008).

# 3. Research findings

## 3.1 General

Water quality varies considerably for upland, rural, agricultural and urban/industrial basins, in terms of average, baseflow and stormflow mean concentrations (Table 2). The major features include an increase in Ca and Gran alkalinity from the upland to the lowland as the influence of bedrock weathering increases. This is because there is a gradual transition down-gradient from older hard-rock areas more depleted in divalent base cations, found in many British upland areas towards lowland sedimentary rocks such as limestone and chalk that are calcareous. There is also enrichment in pollutants such as nitrogen (N) and phosphorus (P), as well as trace metals in the industrial and urban areas. However, for the upland areas, Al, Mn and Fe concentrations are especially high due to the acidic and organic rich conditions. In the case of the upper parts of the Ribble and Wyre, the underlying carbonate rich bedrock ensures that the groundwater inputs to the river are bicarbonate rich. Hence, the streams are not highly acidic, although the concentration of many trace elements of relatively low solubility under circumneutral conditions, such as aluminium (Al), iron (Fe) and titanium (Ti), remained high probably due to the presence of colloidal material (Neal et al., 1997a, 2011a, c, d).

In brief, the main patterns are as follows.

## 3.2 Gran alkalinity, the balancing divalent base cations and the relevance of photosynthesis and respiration to pH.

Within many parts of the UK uplands, a combination and acidic soils and atmospheric pollution and acid mine drainage has led to acidic runoff (Neal et al., 2005c, 2010e, 2011a,d). However, for the UK lowlands, surface waters are generally bicarbonate bearing and of moderate pH (typically, 6 to 9) due to the weathering of minerals within the soil/aquifer matrix bedrock by atmospheric and soil generated $CO_2$. The bicarbonate is balanced mainly by divalent cations (Ca and Mg in particular). For lowland waters, pH can rise up to almost pH 11 for the cleanest of the east coast rivers, the Tweed, due to the dominance of photosynthesis when dissolved $CO_2$ levels can be less than a hundredth that of saturation (Neal et al., 1997b). Correspondingly for the more polluted environments where respiration dominates, $CO_2$ concentrations can be over ten times saturation and pH can be lowered by one unit (Neal et al., 1998). For low Gran alkalinity waters, the $CO_2$ system has little effect on pH as the $CO_2$ is primarily in undissociated form.

## 3.3 Sewage effluent, groundwater sources, end-member mixing and its flux extension

Even for the rural areas there is a fingerprint of sewage contamination in the rivers (Neal et al., 2005b, 2011a; Jarvie et al., 2006a) with enrichment of many elements such as N, P and boron (B). This is most clearly observed under baseflow conditions as STW discharges to the river are least diluted (Figure 2). However, sewage effluents can also be enriched at high flows in rural areas due to the flushing of contaminants associated with septic tanks when the catchment wets up (Neal et al., 2004a,b, 2010a,b). Nonetheless, it is not simply the contaminants that dilute with increasing flow: so to do the weathering components (Figure 2). This occurs because the groundwater is enriched in such components and it is diluted under stormflow condition by near-surface waters that have had insufficient time to equilibrate with the soil/aquifer matrix. Due to this, many elements exhibit linear correlations when plotted against each other (Jarvie et al., 1997; Neal et al., 1997a). This may be described in terms of two-component chemically conservative mixing using End-Member Mixing Analysis (EMMA, Christophersen et al., 1990). Nonetheless, there is also an issue of how long a pollutant may be stored in a catchment both in relation to reservoirs and groundwater. While storage issues cannot be examined based on EMMA, an extension to EMMA based on flux rather than concentration changes provides new insights (Neal et al., 2010a,b; Jarvie et al., 2011). Here the notion is that a simple representation of the mixing system is one where there is a constant flux input of point source effluents and a catchment wide "diffuse" input with a flux directly proportional to the flow increase. For such a system, the gradient ($\delta B_{flux}/\delta flow$) at high flow represents the concentration of the diffuse component.

Across the rivers monitored, a critical effluent marker is B (Neal et al., 2010b, 2011a). This is because B is highly enriched in effluents (the effluent signal to background is large) and B remains in the water column (it is relatively soluble and not readily biodegradable). Further, B concentrations have declined significantly over the past 20 years (as illustrated in Figure 3) and so the relative changes in boron concentration in the stream can be compared with the actual reductions in the input to set against storage within the catchment. A curvilinear relationship between the water and the B fluxes provides a strong indication of local storage such as recharge to the aquifer/gravels at low flows (Neal et al., 2010b). Something similar has been observed for Soluble Reactive P (SRP, which is essentially inorganic monomeric P, i.e. phosphate). However, for SRP there was an additional process of within-river uptake by the phytoplankton and macrophytes as well as water-sediment interactions (Neal et al., 2010a). Due to this, the diffuse B concentration had to be calculated for the higher flow values when more linear patterns are observed and local storage effects are less important. This approach has been applied across our dataset to examine the relationship between the point source signal (here taken as the average of the bottom 10% of flows) and the diffuse source contribution (Figure 4). There are three clear features.

1. For the data collected in the 1990s there is an approximately linear relationship between the baseflow and diffuse concentration. This indicates the importance of contaminant sources to the diffuse signal.
2. For the data collected in the 2000s, a correlation remains between the point and diffuse signal, but the relationship changes to a curvilinear one with a higher diffuse concentration relative to the point source (compared to the 1990s dataset).
3. Where there are data that spans the two decades (the Thames), the change over time is one of a decreasing concentration in point sources but no corresponding change for the diffuse component. For example, in the case of the Thames, between the periods 1997/98 and 2006, B concentrations in baseflow decreased almost by a factor of three (around 330 to around 120 µg/l) and yet the regional B concentration declined only slightly (67 to 59 µg/l).

The results indicate that there is a strong sewage effluent component to the diffuse signal. Further, the results point to the effluent component in the diffuse signal being maintained at the decadal scale even when the effluent inputs reduce during that time. This in turn implies decadal-scale within-catchment storage.

## 3.4 The nutrients

### *3.4.1 Silicon*

An almost universal misnomer in hydrogeochemistry is that common $SiO_2$ minerals (quartz/chalcedony) are inert. However, their surfaces become activated in the presence of dissolved silicon (Si) above mineral saturation and the river waters are generally close to saturation with these minerals (Casey and Neal, 1984; Neal et al., 2005d). Furthermore, when photosynthesis is high and siliceous diatoms are in bloom, the Si levels can decline to less than detection limits and Si may indeed become the limiting nutrient (Neal et al., 2005d).

### *3.4.2 Nitrogen*

The dominant form of nitrogen within the rivers is nitrate ($NO_3$) and catchment sources are dominated by agriculture (Jarvie et al., 1997; Neal et al., 2006e). For the more permeable agricultural catchments there is a limited range in riverine $NO_3$ concentration although concentrations often increase in a gradual way as a function of flow. This pattern results from within-river uptake of $NO_3$ during the spring and the summer when biological activity is high and a seasonal fall in the water table. Further, $NO_3$ concentrations have increased over the last 50 years or more. This primarily reflects increases in fertilizer inputs during the first half of the twentieth century with contamination of the unsaturated, saturated and groundwater zones. Significant within-catchment attenuation and aquifer storage result in long water residence times. This has ensured that more recent reductions in fertiliser application have not translated to major reductions in $NO_3$ within the rivers (Wheater and Peach, 2004; Wheater et al., 2006; Smith et al., 2010) and other factors have come into play such as the influence of two World Wars (Howden et al., 2011). For the low permeability catchments, $NO_3$ concentrations in the rivers generally increase with increasing flow before levelling-off at high flow and in some cases declining at very high flows. This is due a combination of increased uptake of $NO_3$ during the spring/summer low-flow periods when biological activity will be maximal and increased $NO_3$-rich runoff from the land under high-flow conditions. The diffuse component of $NO_3$ for the agricultural catchments is usually greater than 80%. However, effluents can be highly significant for the low permeability cases under baseflow conditions when STW inputs are high and/or denitrification processes are limited. (Neal et al., 2006e, 2011a). Furthermore, atmospheric inputs of N to the catchments may be large. Such N inputs are dominated by ammonia/ammonium-ions ($NH_3/NH_4^-$) which is strongly retained by the catchment (Neal et al., 2004b). While reduced-N ($NH_3/NH_4^+/NO_2^-$) may be of low concentrations within the rivers, they have relatively high toxicity and are of environmental concern.

### *3.4.3 Phosphorus*

Phosphorus in rivers occurs in dissolved and particulate forms. Of the soluble forms, inorganic P (SRP) dominates, but organic, inorganic-polymeric and colloidal components (DHP) can be significant especially in the more rural areas (Neal et al., 2010d). SRP generally correlates with effluent markers such as B and with population density indicating the importance of sewage sources (Davies and Neal, 2004, 2007; Neal et al., 2005b; Jarvie et al., 2006a). SRP concentrations mainly dilute with increasing flow as the effluent sources become dominant. However, for the more rural areas, SRP concentrations sometimes increase with increasing flow as diffuse inputs from septic tanks and agriculture are flushed from the catchment as it wets up. Within the river, there are interactions between the water, sediment and biota, with partial removal of SRP from the water column in the growing season. Further, there may be enhanced SRP loss for basins with reservoirs as storage times can be especially long and the linkage between SRP and B can then be much reduced (Neal et al., 2011a). For many UK rivers there has been a major reduction in SRP concentrations due to removal of SRP in effluents for the main sewage treatment works since the late 1990s (Neal et al., 2010a; Bowes et al., 2010). Nonetheless, the reductions may well be less than expected due to contaminated groundwater storage, with interchange to/from the river (Neal et al., 2010a). This pattern is very similar to that for B although the use of flux extended end member mixing indicates a more complex/erratic behaviour with change in flow as it seems that there are several types of store within the catchment that are released to the river during rainfall events (Neal et al., 2010a, 2011a; Jarvie et al., 2011). Further, during the initial phase of reduction there may be a net release of P from the contaminated sediments (Jarvie et al., 2006b).

### *3.4.4 Biological response to phosphorus reduction*

Within UK rivers, P is often assumed to be the limiting nutrient for plant and algal growth. Therefore, great efforts have been made to reduce SRP concentrations within effluents for larger STWs and the associated financial costs have been high (Neal et al., 2010d). The assumption has been that high SRP concentrations have led to symptoms of ecological damage (such as excessive plant and algal growth and low night-time dissolved oxygen concentrations) within rivers. Agricultural and STW sources have both been implicated by increasing SRP loading to the rivers. Indeed, poor biological status in rivers is often (wrongly) taken as synonymous with SRP loadings. Further, not all parts of the aquatic food chain are considered within such assessments and P can be biologically significant in forms other than SRP (organic + polymeric + colloidal P) at relatively low P concentrations, but in many studies these are not monitored (Neal et al., 2010d; Whitton and Neal, 2011).

For the surveys covered in this paper, river biology has not been monitored other than indirectly based on chlorophyll-a measurements and anecdotal evidence for macrophytes in the case of the River Kennet. Chlorophyll-a may be considered a surrogate for phytoplankton (Neal et al., 2010c). The data indicate strong seasonal variations across the rural to agriculturally impacted sites with concentrations peaking in the spring and summer time when biological activity is at its highest (Pinder et al., 1997; Neal et al., 2006d). There are large variations in the magnitude of the seasonal effects across the rivers and for the spring/summer low-flow periods average concentrations of chlorophyll-a correlate with SRP. At first sight it seems that the high SRP levels promote algal growth thereby increasing phytoplankton levels. However, both chlorophyll-a and SRP concentrations peak when temperatures are high and water flows are low (Jarvie et al., 2004). Thus, under these conditions there are two different types of driver: increased biological activity linked to physical conditions within the river and low dilution that ensured high SRP concentrations from effluent sources. A strong correlation between chlorophyll-a concentration and catchment area has been observed (Neal et al., 2006d). Further, the relationship splits with the highest chlorophyll-a concentrations (for a given catchment area) being associated with sites with water inputs from reservoirs and canals. The chlorophyll-a distribution probably links to temperature and water residence time, and is enhanced by phytoplankton inoculation from the reservoirs and canals. Further, planktonic and algal growth rates are also affected by light levels, numbers of zooplankton that graze on the phytoplankton and attached algae, and the density of invertebrates that feed on the attached algae. In the case of the industrial rivers, organic pollutants such as herbicides can be high (House et al., 1997; Long et al., 1997) and this may inhibit phytoplankton growth (Neal et al., 2006d). Indeed cleanup of herbicides in the industrial rivers may even lead to increased eutrophication issues.

Many UK rivers are significantly affected by river and water management. For example, abstractions for water supply and river straightening change the flow regime of the river. Further, bank-side clearance of trees increases light levels and temperature. Such changes affect the functioning of the river ecosystem and can destroy bank-side refuges for the zooplankton and invertebrates. Superimposed on this are the effects of high fish stocking levels designed to enhance the fishing amenity value of many of our rivers, and impoundments/sluices which reduce flow velocities, promoting algal growth. The fish feed in part on the zooplankton and invertebrates that feed on the phytoplankton and invertebrates. The net effect of the increased management of the rivers has thus been to increase algal development. It is therefore not appropriate to simply target SRP as either the culprit or the potential saviour if SRP levels can be reduced. Further, there is the issue of reducing pollutant levels for a mixture of contaminants. This may affect the ecosystem in different ways dependent upon what part of the food chain is affected. Whatever the process, many of the UK rivers are managed and cannot be viewed in terms of "natural" water bodies.

The highly managed upper Thames Basin provides a good example of these effects. A campaign to reduce SRP from a local STW resulted in a marked reduction in SRP within the river, but it did not lead to an improvement in stream biology with regards to macrophytes and algae (Jarvie et al., 2002). Rather, the river became devoid of macrophytes after the development of epiphytic coverings. Further, the situation remains poor over a decade after the P stripping at the STW. Thus, the ecosystem has not responded with the anticipated improvement. Nonetheless, within the river reaches there was a large variation in the macrophyte levels and the health of the river. Hence, there may well be a number of physical factors that are determining damage that remain to be resolved. What the impacts are on other types of stream biota remains unknown. Riverine biology is not simply confined to algae and macrophytes and the various components to the ecosystem functioning need to be considered in conjunction (e.g. zooplankton, invertebrates, fish, etc.).

## 3.5 Trace metals

For the urban and industrially impacted systems there is enrichment in a number of trace metals. Contamination is not simply confined to components originating in present day effluents. For example, in the upper parts of the River Swale in the Humber basin, the waters are relatively enriched in barium (Ba) and lead (Pb). This is indicative of flood-plain contamination from mining activities of the North Pennine ore-field from Roman times to that of the Industrial Revolution of the 18$^{th}$ and 19$^{th}$ centuries (Hudson-Edwards et al., 1997; Macklin et al., 1997; Neal et al., 1997a). Further, there is also metal enrichment of transition metals such as cadmium (Cd), chromium (Cr), cobalt (Co), manganese (Mn), molybdenum (Mo) and nickel (Ni) as well as arsenic (As), lithium (Li) and rubidium (Rb) within the urban/industrial areas

(Neal et al., 1997a). For the lowlands of the Ribble, many of the contemporary trace element concentrations are close to or below 1 µg/l (Neal et al., 2011a). The dissolved phase component is based on an operational measure of 0.45 µm filtration. However, within this component there may well be colloidal material especially in the case of easily hydrolysable metals (Neal et al., 1997a, 2011a,c,d). There is a clear distinction between the downstream river stretches close to point source discharges and upstream where river concentrations are driven by diffuse inputs. For example, in agricultural drains and in river water close to STWs, samples contain only 10% of trace elements as colloids whilst upstream the percentage is around 40-50% (Rowland et al., 2011). For the industrial and urban areas, there is a complex relationship with flow for many elements as there may well be a number of diffuse and point sources. However, in the case of As (Rowland et al., 2011) and Li, Rb and Mo (Neal et al., 1997a), their concentrations dilute with increasing flow and point sources are strongly implicated.

### 3.6 River water quality may be generally improving

There has been a long-term clean-up that links to both the striving of the UK environment agencies and the change in economic conditions towards a post-industrial setting (Neal, 2001).

There has been a large reduction in the emissions of metals to the atmosphere, especially since the 1990’s. For example, mercury (Hg) emissions declined from 36 t/yr in 1992 to 7.2 t/yr in 2010 (Rowland et at 2010a). Therefore the impact of wet deposition inputs to rivers has declined and is more directly related to leaching of metals complexed to and transported with dissolved organic carbon (DOC) (Rowland et al., 2010b). Correspondingly, there have been major reductions in atmospheric emissions of acidic oxides as the relevance of “acidic deposition” was fully recognised (UKAWRG, 1988).

In the case of B and SRP, we have directly observed reductions over time. For the toxic metals, discharges from STWs appear to be significant for Hg and Ni but not for Pb and Cd. The current risk associated with diffuse and point source inputs of the priority substances associated with the Water Framework Directive is low. Rowland et al. (2010c) found no annual average concentrations of dissolved Pb, Cd, Ni and Hg (Rowland et al., 2010b) in the Ribble and Wyre catchment above the regulatory Environmental Quality Standard values, and neither were there any values exceeding the defined maximum allowable concentrations. Comparing more recent data for the Ribble and Wyre (Neal et al., 2011a) with earlier studies of the eastern UK rivers (Neal and Robson, 2000; Neal and Davies, 2003) indicates that pollutant concentrations have generally declined over the past 20 years when considering similar catchment typologies.

This trend fits well with observations from earlier studies due in large part to the proactive approach of UK environmental protection agencies (Currie, 1997; Edwards et al., 1997).

## 4. Conclusions

The data provided here are extensive both in terms of the number of water quality determinands and coverage of the major lowland landscape types (rural, urban, industrial and agricultural catchments). They indicate a variety of key mechanisms that determine the water quality of British lowland rivers. These comprise within-catchment and effluent sources that are attenuated by flow (e.g. dilution of point sources), water residence time (storage) and biological uptake/release. The within-catchment diffuse sources include both weathering and pollutant components. For some pollutants there is probably significant storage that can partially buffer any reduction in pollutant loading, even though point-source reductions may be more immediate. This is important when dealing with timescales for achieving water quality and ecological improvements, where effluent and agricultural sources are being targeted for reduction. For example, in the case of N and P concentration reductions, reductions in the sewage effluent discharging to rivers are much more likely to produce a rapid concentration reduction in the river, whereas reductions in pollution from agricultural diffuse sources and mediation from within-catchment water storage can lead to delays of decades before improvements in lowland river water quality are achieved. Of particular significance is the ‘legacy’ of pollution in catchments and the time lags and hysteresis associated with re-equilibration of catchment ecosystems, following the introduction of remediation measures or the changeover from an industrial to a post-industrial setting.

The Water Framework Directive is shaping European environmental policy and, commendably, the emphasis is being placed on improving aquatic biological status. However, the issues are multifaceted and it may well be that a focus has been unduly placed on dealing with just one given pollutant in isolation. For example, reducing herbicides may even result in increased eutrophication for nutrient contaminated rivers. From a socioeconomic standpoint, resolving such issues is of strategic importance in relation to the cost of removing pollutants from effluents or the land and reducing the sustainability of fragile farming communities. Further, our studies suggest that overemphasis has been placed on farming impacts, at least with regards to P (Neal et al., 2010d). However, there may well be some significant farming-related issues such as high sediment runoff from disturbed land when the catchments wet up and rapid surface/sub-surface flow dominates. Our work implicates point sources of P, and critically such sources may well become even more important due to the continued growth in UK population. This issue may be exacerbated by extended periods of low flows and reduced dilution potential within rivers. Such extended low-flow periods may link directly to increased water demand from the rising population and food security with increased agricultural usage. It may also be indirectly linked to climate change and climate instability due to increased and erratic periods of atypically low rainfall.

In our studies, there has been a lack of biological measurements and while this is unfortunate, the costs and practical arrangements for sampling were simply too large. However, in assessing biological recovery, there are three types of constraint that have not been resolved that make targeting and timings difficult.

1. Very few UK aquatic environments can be considered as pristine ‘reference conditions’ and most water bodies have been modified in some ways (river straightening, reductions in flow, loss of bank-side habitat, etc.) and it is not clear what if any environmental targets should be set.
2. Short and longer term climate instability and variability affects the seasonal distribution and intensity of rainfall and low and high flows within the river as well as

temperature and light distributions. This in turn impinges on the biological functioning within the river.
3. There are issues of how the pollutants affect biology and ecosystems that potentially have large and complex feedback loops.

Therefore, it is not at all clear that simply reducing a pollutant will result in a change back to the conditions that prevailed prior to its introduction. This is particularly apparent in the UK, with long legacies of industrial and agricultural activity. Pollutants may have been introduced to the river hundreds or even thousands of years ago. Rather, improving physical habitat may hold the key to improving ecological status, particularly for rivers.

This paper has drawn upon large archives from UK NERC strategic research programmes. The ongoing analyses of these data, and combination with major archive data collected by regulators for other purposes, provide a major national evidence base with which to tackle the many major challenges in environmental management. The examples of general principles which have emerged from these studies represent a small part of the total knowledge to be harvested from these data sources. We hope that the data and corresponding references provide a resource to environmental scientists, educators and environmental managers for many years to come.

## Acknowledgements

The data contained in this study has resulted from considerable input by many field and analytical workers across CEH. Over the years, a large number of analysts and field workers have been involved in the study that are worthy of mention. The list is too great to present here, but their efforts have been recognised within the authorship of many of the papers cited in this presentation.

Colin Neal gives profound thanks to all who have supported the publication of this work and data resource that he striven for up to his retirement.

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# Tables.

Table 1. Catchment monitoring periods and catchment types: R=Rural, A=Agriculture, I=Industrial, U=Urban and M=Mining. STW = Sewage Treatment Works effluents.

| River | Sites | Type | Start date | End date | River | Sites | Type | Start date | End date |
|---|---|---|---|---|---|---|---|---|---|
| | | **Tweed Basin** | | | | | **Thames Basin** | | |
| **Tweed** | 3 | R | 23-Aug-94 | 17-Feb-97 | **Thames** | 1 | R/A | 09-Apr-97 | 28-Mar-07 |
| | | | | | **Cherwell** | 3 | R/A | 26-Jul-00 | 12-Jun-02 |
| | | **Wear Basin** | | | **Ray** | 1 | R/A | 26-Jul-00 | 11-Dec-01 |
| **Wear** | 1 | R/M | 01-Oct-97 | 13-Oct-98 | **Thame** | 3 | R/A | 26-Jul-00 | 28-Mar-07 |
| | | | | | **Dun** | 6 | R/A | 02-Oct-00 | 21-Oct-08 |
| | | **Humber Basin** | | | **Froxfield** | 1 | R/A | 02-Oct-00 | 02-Jan-02 |
| **Aire** | 1 | U/I | 07-Sep-93 | 11-Feb-97 | **Kennet** | 11 | R/A | 03-Jun-97 | 21-Oct-08 |
| **Calder** | 1 | U/I | 07-Sep-93 | 16-Dec-96 | **K&A Canal** | 8 | R/A | 02-Oct-00 | 27-Oct-09 |
| **Derwent** | 1 | A | 07-Sep-93 | 16-Dec-96 | **Crofton Res** | 1 | R/A | 02-Oct-00 | 02-Jan-02 |
| **Don** | 1 | U/I | 07-Sep-93 | 11-Feb-97 | **Shalbourne** | 1 | R/A | 02-Oct-00 | 02-Jan-02 |
| **Nidd** | 1 | R | 07-Sep-93 | 16-Dec-96 | **Lambourn** | 3 | R/A | 10-Apr-02 | 27-Mar-07 |
| **Ouse** | 2 | R | 01-Sep-94 | 18-Feb-97 | **Pang** | 9 | R/A | 22-Jul-97 | 27-Mar-07 |
| **Swale** | 2 | R | 07-Sep-93 | 16-Dec-96 | **STW** | 8 | | 24-Oct-00 | 27-Oct-09 |
| **Trent** | 1 | U/I | 07-Sep-93 | 11-Feb-97 | | | | | |
| **Ure** | 1 | R | 07-Sep-93 | 16-Dec-96 | | | **Ribble Basin** | | |
| **Wharfe** | 1 | R | 07-Sep-93 | 18-Feb-97 | **Ribble** | 6 | R/U/I | 18-Feb-08 | 22-Mar-10 |
| | | | | | **Calder** | 5 | R/U/I | 18-Feb-08 | 22-Mar-10 |
| | | **Great Ouse Basin** | | | **Douglas** | 7 | R/U/I | 18-Feb-08 | 22-Mar-10 |
| **Great Ouse** | 1 | A | 13-May-97 | 07-Jul-98 | | | | | |
| | | | | | | | **Wyre Basin** | | |
| | | | | | **Wyre** | 7 | R/A | 18-Feb-08 | 22-Mar-10 |

Table 2. Averages and average baseflow and stormflow concentrations, for an upland (Tarnbrook Wyre), a rural (Tweed), an agricultural (Great Ouse) and an urban/industrially impacted river (Don).

| | | Upland | | | Rural | | | Agriculture | | | Urban/industrial | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Avg | Base | Storm | Avg | Base | Storm | Avg | Base | Storm | Avg | Base | Storm |
| Na | mg/l | 6 | 6 | 5 | 11 | 15 | 8 | 62 | 83 | 28 | 109 | 144 | 56 |
| K | mg/l | 0.7 | 1.0 | 0.7 | 1.5 | 2.0 | 1.4 | 11.5 | 14.6 | 6.2 | 11.0 | 14.9 | 6.5 |
| Ca | mg/l | 4 | 5 | 3 | 35 | 40 | 23 | 133 | 125 | 128 | 64 | 70 | 48 |
| Mg | mg/l | 1.3 | 1.8 | 0.9 | 10.6 | 16.1 | 5.4 | 8.5 | 8.8 | 7.4 | 23.1 | 23.5 | 15.8 |
| Cl | mg/l | 9 | 9 | 9 | 19 | 26 | 15 | 83 | 106 | 51 | 135 | 159 | 84 |
| $NO_3$-N | mg/l | 0.3 | 0.2 | 0.4 | 1.5 | 1.2 | 1.6 | 8.4 | 6.1 | 10.7 | 7.7 | 9.0 | 5.8 |
| $SO_4$ | mg/l | 6 | 7 | 9 | 12 | 17 | 9 | 144 | 163 | 101 | 161 | 196 | 102 |
| SRP | µg/l | 6 | 4 | 13 | 37 | 31 | 27 | 1584 | 2330 | 430 | 1624 | 2765 | 360 |
| $SIO_2$ | mg/l | 3.6 | 2.8 | 2.8 | 2.7 | 0.9 | 4.0 | 3.1 | 3.1 | 3.6 | 8.0 | 7.0 | 8.0 |
| DOC | mg/l | 7.6 | 4.2 | 9.2 | 4.0 | 2.6 | 6.6 | 5.7 | 6.0 | 7.1 | 5.9 | 7.2 | 5.4 |
| pH | | 7.1 | 7.8 | 6.3 | 8.24 | 8.37 | 8.45 | 8.03 | 8.00 | 8.01 | 7.58 | 7.64 | 7.54 |
| ALK | µEq/l | 140 | 340 | 40 | 2223 | 2746 | 1487 | 4377 | 4302 | 4269 | 2188 | 2641 | 1558 |
| Al | µg/l | 141 | 35 | 209 | 46 | 7 | 156 | 8 | 3 | 25 | 23 | 20 | 64 |
| B | µg/l | 9 | 13 | 7 | 23 | 45 | 11 | 387 | 554 | 132 | 462 | 714 | 152 |
| Ba | µg/l | 24 | 24 | 24 | 95 | 123 | 57 | 25 | 19 | 32 | 22 | 16 | 27 |
| Fe | µg/l | 368 | 213 | 401 | 56 | 13 | 148 | 27 | 24 | 37 | 91 | 49 | 144 |
| Li | µg/l | 3 | 3 | 2 | 2 | 4 | 1 | 13 | 14 | 10 | 31 | 36 | 15 |
| Mn | µg/l | 21 | 9 | 34 | 7 | 7 | 6 | 5 | 2 | 9 | 257 | 157 | 222 |
| Sr | µg/l | 15 | 22 | 11 | 117 | 164 | 64 | 493 | 502 | 444 | 222 | 251 | 137 |
| Zn | µg/l | 5 | 2 | 8 | 8 | 4 | 4 | 11 | 24 | 6 | 28 | 22 | 16 |

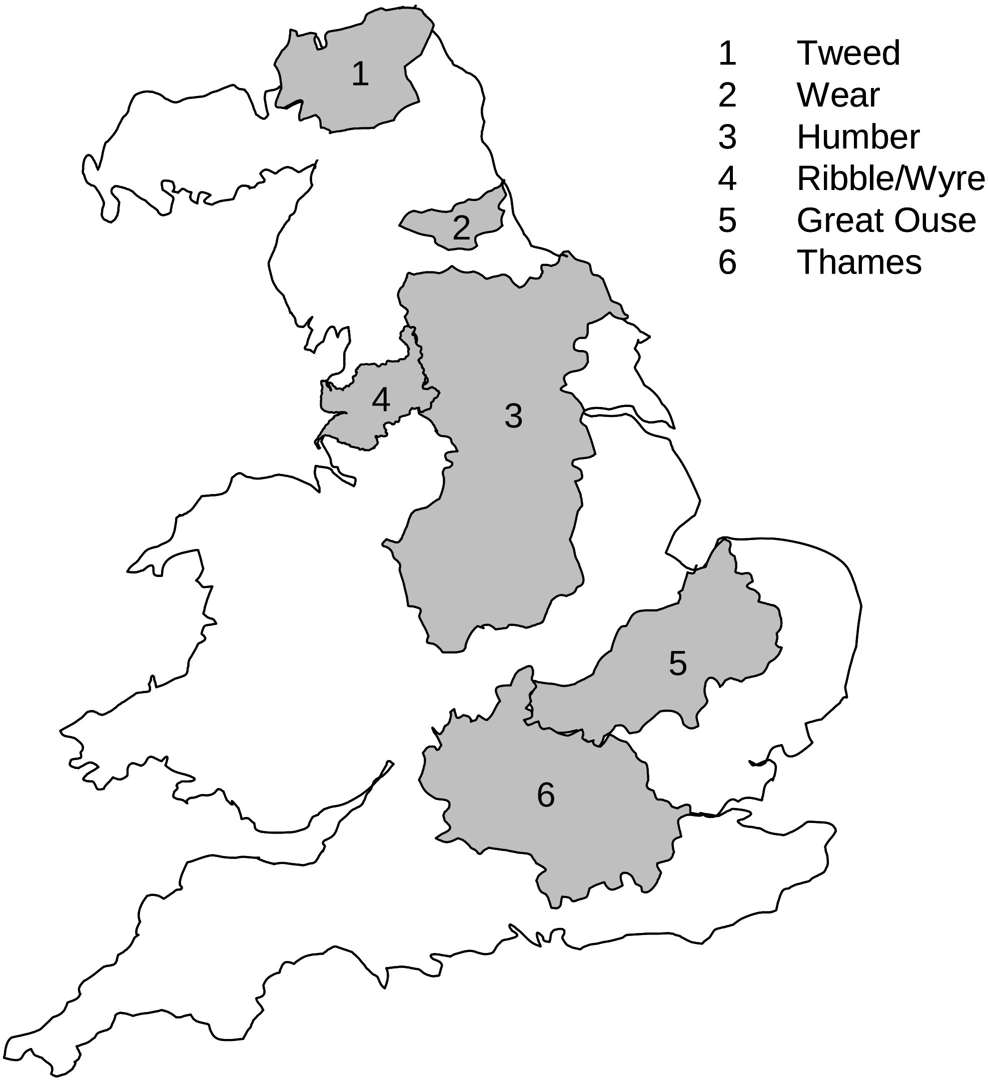
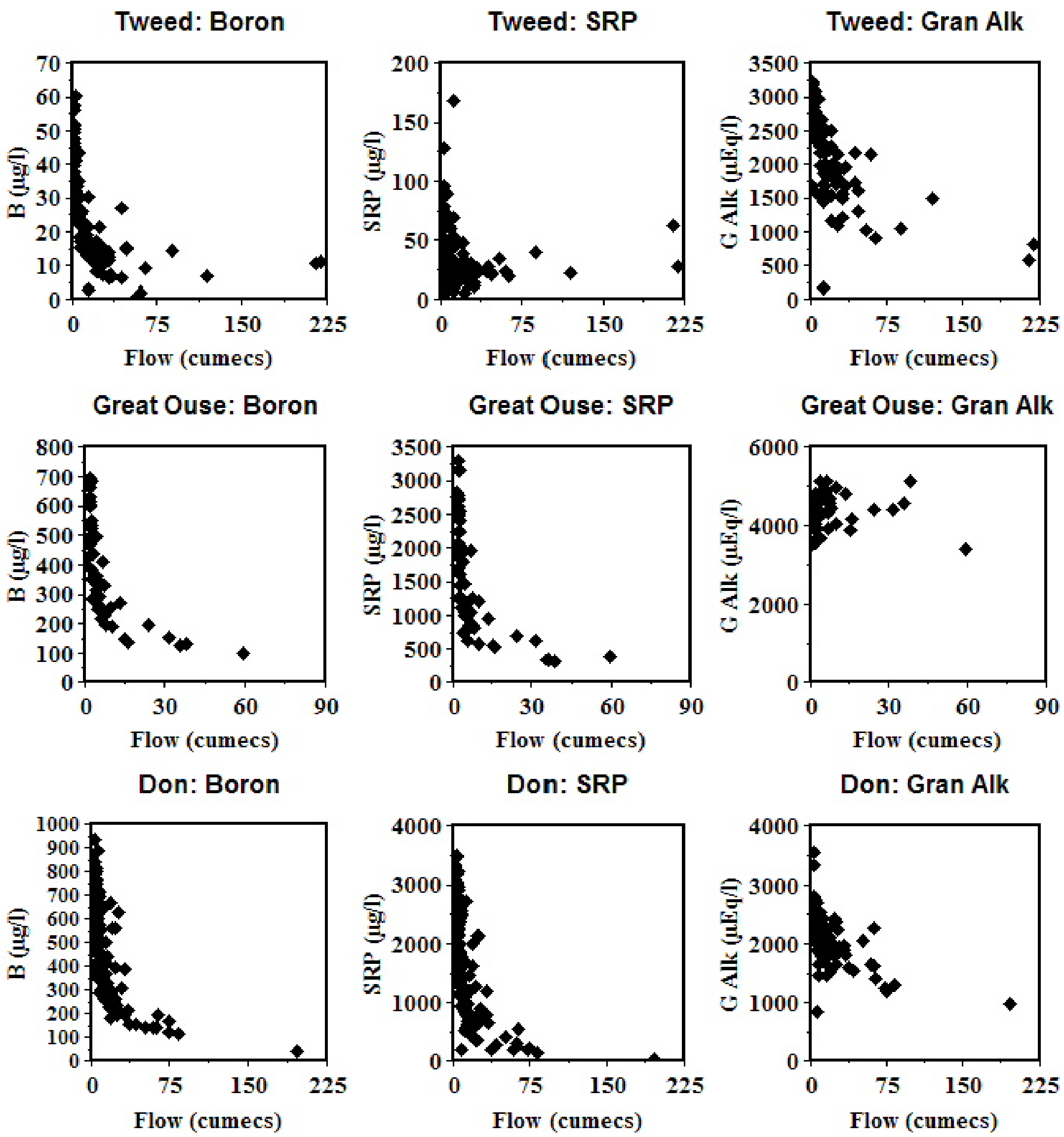



Figure 1. The monitoring areas.

Figure 2. The relationship of B, SRP and Gran Alkalinity with flow for rural (Tweed), agricultural (Great Ouse) and urban/industrial (Don) impacted rivers.



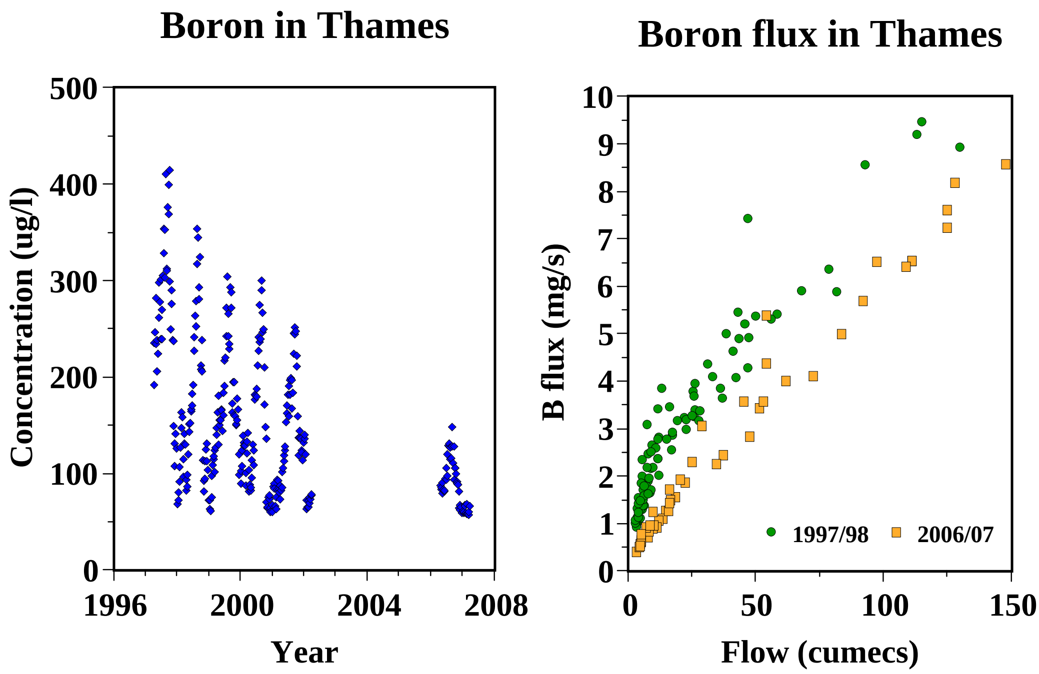



Figure 3. Boron concentration changes in the River Thames and the relationship between water and boron flux.

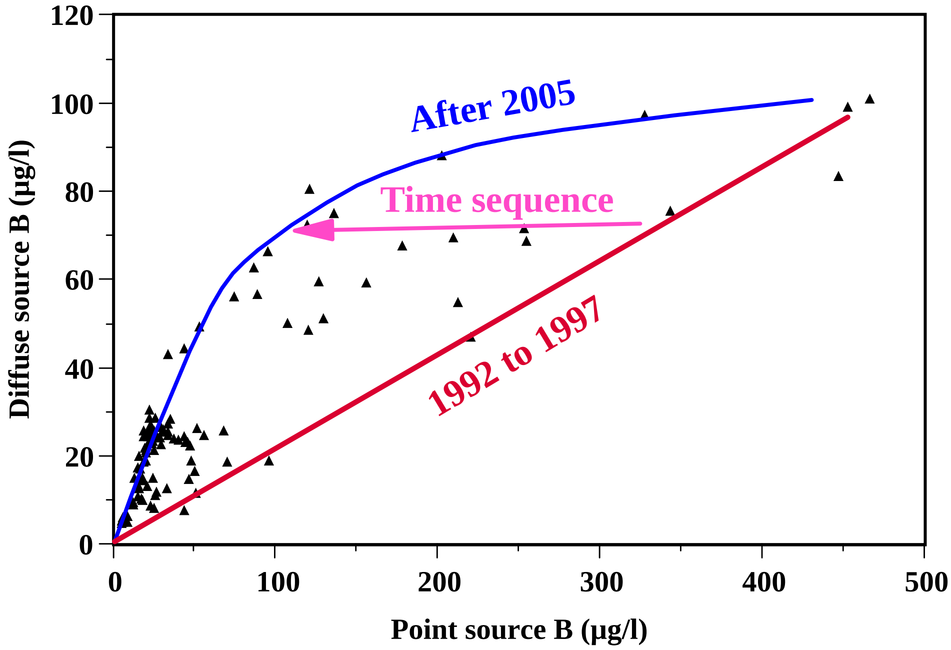



Figure 4. The relationship between baseflow and diffuse B concentrations for UK rivers as monitored during various monitoring periods 1992 to 2010.