Science of the Total Environment 408 (2010) 1315–1330

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Declines in phosphorus concentration in the upper River Thames (UK): Links to sewage effluent cleanup and extended end-member mixing analysis

Colin Neal [a,*], Helen P. Jarvie [a], Richard Williams [a], Alison Love [b], Margaret Neal [a], Heather Wickham [a], Sarah Harman [b], Linda Armstrong [a]

[a] Centre for Ecology and Hydrology, Maclean Building, Crowmarsh Gifford, Wallingford, OXON, OX10 8BB, UK
[b] Environment Agency. Red Kite House, Howbery Park, Wallingford, OXON, OX10 8BD, UK

ARTICLE INFO

Article history:
Received 16 June 2009
Received in revised form 19 October 2009
Accepted 19 October 2009
Available online 17 November 2009

Keywords:
River
Thames
Phosphorus
Sewage
Agriculture
Endmember mixing analysis
Phosphorus stripping
WFD

ABSTRACT

Phosphorus concentrations in the upper River Thames Basin (southeastern England) are described and linked to sewage effluent sources. Weekly surveys between 1997 and 2007 of the Thames and two of its major tributaries, the Thame and the Kennet indicated that phosphorus was mainly in soluble reactive (SRP) form. Baseflow concentrations in the Thames reduced from 1584 μg/l in 1998 to 376 μg/l in 2006 and from 2655 to 715 μg/l for the Thame. Flow response, flux and endmember mixing analysis indicated that these declines resulted from SRP reductions in sewage treatment works (STW) effluent following phosphorus stripping for the major STWs in the region. This was confirmed by comparing our analysis with direct measurements of SRP in the effluents based on Environment Agency data. A within-river loss under baseflow of ~64% (range 56–78%) of the SRP-effluent input was estimated for the Thames, with a near balance for the Thame. SRP concentrations in the Kennet were an order of magnitude lower than the Thames/Thame: non-point sources dominated and were important for all the rivers at high flows. It was concluded that removal of SRP from effluents would be insufficient SRP in the Thames and Thame to meet annual average environmental targets of 50 to 120 μg/l.

The paper flags the value of combining hydrological/chemical tracing and concentration/flux approaches to data interrogation and the bonus of having actual measurements of the effluent. It highlights the need for fuller assessment of water storage/sediment/biota interactions for phosphorus and for caution in using boron as a long-term tracer for effluent inputs, its concentrations having declined markedly in response to reduced usage in washing powders: the value of using sodium as a tracer for examining SRP changes is shown.

1. Introduction

The importance of phosphorus pollution to eutrophication in many European rivers is recognised within the context of the Water Framework Directive (Billen et al., 2007a; CEC, 2000; Mainstone and Parr, 2000, 2002; Mainstone et al., 2000; Withers and Lord, 2002). Indeed, the issue is of global concern in relation to environmental sustainability in terms of agricultural, urban and industrial sources (Malmqvist and Rundle, 2002; Mallin and Cahoon, 2003; Collins and McGonigle, 2008; Dodds et al., 2009). Within the UK, the trophic state of many rivers and lakes is controlled by phosphorus concentration (Hilton et al., 2006) and eutrophication associated with pollutant sources is believed to be widespread (White and Hammond, 2009). The issue is no longer one of "is there a problem?" Rather, it is of "where is the problem" and what are the most cost effective environmental management strategies that can be put in place to produce the desired improvement in river ecology. A major focus for remediation is on areas where there are issues of urban/industrial inputs of effluents and intensive agricultural inputs (or some combination of both). Nonetheless, the concentration of phosphorus needed to eliminate eutrophication risk remains uncertain although "pragmatic" management is being set. For example, in the UK, the targets vary from annual averages of 20 to 120 μg/l in relation to standards of "high" and "good" water quality as linked to the catchment typology and the alkalinity of the water (Mainstone and Parr, 2002; WFD UK TAG, 2008), but there remains issues on the importance of other drivers and other nutrients (Moss, 2008).

Here, the phosphorus levels within a major UK basin, the Thames, are examined where there are major issues of eutrophication associated with high phosphorus loadings and eutrophication (Kinniburgh et al., 1997; Young et al., 1999; Kinniburgh and Barnet, in press). Problems associated with phosphorus are being intensified due to increasing population, agricultural intensification, increased water consumption and predicted declines in rainfall (Rodda, 2007). Reductions of soluble reactive phosphorus (SRP; also sometimes termed phosphate and orthophosphate) have taken place within many UK rivers over the last decade as phosphorus stripping at sewage treatment works (STW) has progressed

* Corresponding author. Tel.: +44 01491 838800; fax: +44 01491 692424.
E-mail address: cn@ceh.ac.uk (C. Neal).

0048-9697/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2009.10.055

in line with the Environment Agency of England and Wales (EA) Asset Management Plans. For this, the European Urban Wastewater Treatment Directive (UWWTD: 9/271/EEC, CEC, 1991) sets a standard where total phosphorus in the effluent must either meet strict concentration limits dependent upon the population equivalent of the STW or remove 80% of the incoming phosphorus. The limits in final effluent set were 2000 μg/l for STWs of 10,000 to 100,000 population equivalent and 1000 μg/l for STWs over 100,000, (Kinniburgh and Barnet, in press). With a major investment in STW infrastructure, the move towards UWWTD compliance is clearly observed for the Thames where effluent discharges of phosphorus have reduced from 5755 to 688 kg-P/day within the last twenty years (Kinniburgh and Barnet, in press).

A major and highly topical issue for the UK is deciding the relative quantities of phosphorus from direct STW effluent discharges to the river and diffuse sources especially during the spring–summer period that is critical for eutrophication with high biological activity and low dilution of phosphorus inputs from effluent sources (Jarvie et al., 2006a; Bowes et al., 2008). Indeed, one critical challenge is to putting diffuse water pollution from agriculture in the context of pollution from other sectors with a move towards a more holistic approach to understanding and managing pressures and impacts (Collins and McGonigle, 2008). For the Thames, assessing the relative importance of these two types of input is crucial to environmental management of many UK and European basins. There is also a need to balance the differing and often competitive needs of population growth, agricultural change, socioeconomics, amenity resource, "invasion of the green belt" and environmentalism (Evans et al., 2003). There are many reasons for a UK focus on the Thames. For example, on the research front there is extensive environmental information for the Thames (Neal et al., 2002a; Jarvie et al., 2002a) including biological surveys and modelling activities (Flynn et al., 2002; Wheater et al., 2006; Wade et al., 2001, 2002a,b, 2008; Whitehead and Williams, 1984; Whitehead et al., 2006; Wilby et al., 2006) and invaluable regulatory information and water quality database of the EA (Kinniburgh and Barnet, in press). Further, the Thames basin is of major importance in terms of size, population, agriculture, climate and effluent change. Hence, the Thames represents a major UK basin for examining phosphorus remediation both in relation to both effluent and agricultural sources. Indeed, there are high social and economic costs associated with complying with the WFD needs. For example, at a national level, the effluent cleanup for England and Wales amounted to around £950 million over the past fifteen years (Kinniburgh and Barnet, in press), while there are major implications for agricultural livelihoods especially when linked to changes in the European Union's Common Agricultural Policy (CAP) reforms (Bateman et al., 2006). The present study contributes new information to this debate and complements research for national and international basin-wide studies (Gren et al, 2000; Salomons, 2004; Billen et al., 2007b), representing a key typology of an urban/agricultural typology with a high regional population density (425 people/km^2). It also builds on earlier studies for the upper Thames (Neal et al., 2000a, 2002a,b, 2004, 2005a,b, 2006a,b, 2008) by providing further indications of changing phosphorus levels as linked to hydrochemical analysis over a longer monitoring period.

Within the study, the changing influence of phosphorus in the effluent (predominantly soluble reactive phosphorus, SRP) is examined in relationship to the changing patterns of SRP concentration changes with respect to flow and with respect to chemical markers within the effluent. This approach is known as endmember mixing analysis (EMMA; Christophersen et al., 1990). Sewage effluents are enriched in several major ions such as sodium, chloride and sulphate as well as SRP (Neal et al., 2005a) and so their concentrations often decline within rivers as flow increases where there are direct effluent inputs to the river (Jarvie et al., 1997). Also, plots of SRP against these markers have often shown linear relationships that are characteristic of chemically conservative mixing of effluent and within-catchment sources provided that the effluent and within-catchment endmembers are of constant concentration (Jarvie et al., 1997; Neal et al., 2005a). Correspondingly, when SRP concentrations have been reduced from within the effluent, then a new linear mixing line has been observed that diverges from the previous linear mixing line at high effluent marker and high SRP concentrations (Neal et al., 2005a). Previously, emphasis has been given to boron as the sewage marker by us. This is because boron is largely supplied from household detergents (it is used as a whitening agent) that enter the river via sewage effluent and boron provides a relatively large effluent to background catchment signal (Neal et al., 1998, 2005a; Jarvie et al., 2006a). Despite this, in recent years boron has declined in concentration in the rivers due to a reduction in its use in household detergents (Neal et al., 2010) and while boron remains a valuable effluent tracer, for the endmember mixing analysis employed here it is potentially deficient when examining long-term data sets as it does not represent a long-term constant boron input to set against examining changes in SRP inputs from the effluent. In this paper we explore the mixing relationships to examine if simple mixing relationships hold for the full data record and to assess the levels of SRP reduction in the river following phosphorus removal from sewage effluent in the Thames Basin. For this we use an alternative tracer to boron, sodium, that is enriched in the effluent and which shows no indication of a pattern of decline within the Thames and its tributaries (Neal et al., 2010). For comparative purposes, data on boron is also presented to indicate what discrepancies might occur with the use of EMMA. Of importance to analytical methodologies for interrogating mixing relationships, EMMA is extended to consider flux as well as concentration changes.

2. Study area and sampling

The Thames is located in the southeastern corner of the UK. In this study the upper half of the basin has been monitored for the main stem and several of the tributaries (Fig. 1). Monitoring was weekly to fortnightly spanning the summer of 1997 to the spring of 2007, with some monthly to yearly gaps.

The main stem of the Thames was sampled near Wallingford at Howbery Park (catchment area ~3500 km^2). Monitoring began in 1997 and continued to spring 2002: it then began again in spring 2006 and continued to spring 2007. Here the Thames catchment is rural with an urban/light-industrial base at towns such as Oxford, Aylesbury, Thame and Swindon. The bedrock is mainly of permeable Chalk and low permeability clays and the river is mainly supplied from groundwater sources (baseflow index, BFI = 0.64): rainfall and runoff averages 715 and 216 mm/year, respectively. As well as the main stem of the Thames two tributaries, the Thame and the upper reaches of Kennet were monitored.

The Thame was sampled at Wheatley from summer 1998 to the spring of 2002 and then from spring 2006 to spring 2007 (catchment area 534 km^2, at the monitoring point). The Thame's catchment typology is largely rural/agricultural with the main populations being at the towns of Aylesbury and Thame; the geology is largely clays/sandstones with some limestone. Rainfall and runoff averages for the Thame catchment are 655 and 230 mm/year, respectively while BFI = 0.59.

The upper reaches of the Kennet (area ~42 km^2) were monitored from summer 1997 and are continuing to be monitored. The Kennet monitoring centred on the town of Marlborough and its STW that discharge directly to the river and which had tertiary phosphorus stripping introduced in 1997. There were two monitoring sites for water quality on the Kennet sites: upstream of Marlborough STW (Clatford) and downstream (Mildenhall). The Kennet is primarily sourced from an underlying Chalk aquifer: rainfall and runoff at Marlborough is 828 mm and 195 mm, respectively, and the baseflow index is 0.94.

3. Chemical analysis and data resource

The waters were sampled for major, minor and trace elements (methods given in Neal et al., 2000a). For phosphorus, three operationally defined measurements were taken using colorimetric phosphomolybdic acid based methodologies. (1) Soluble Reactive Phosphorus (SRP,