

# Copper in the Thames Estuary in relation to the special protection areas

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**Abstract** Copper poses a risk to the integrity of the Thames Estuary and Marshes special protection area (SPA) as bioaccumulation within the food chain takes place. This article describes some of the investigations carried out for the Habitats Directive Review of Consents including a review of the methods used to analyse copper samples; analysis of the long-term data sets gathered by the Environment Agency; and modelling work. Mean dissolved copper levels for 2002–2006 are below the 5 µg/l Environmental Quality Standard. Catchment modelling was used to establish total copper budgets both for sources discharging directly to the Tideway and for sources throughout the Thames catchment including sewage treatment works (STWs), industries, non-urban, and urban runoff. The total copper load to the Tideway was estimated to be 36 tonnes/year with 52% of this attributed to STWs. Modelling was used to explore the mixing, transport and fate of copper throughout the estuary taking account of partitioning and the

interaction with sediments. The modelling showed how the fourth Water Industry Asset Management Programme (AMP4) improvements to the main London STWs would affect copper concentrations throughout the estuary.

**Keywords** Copper · Marine waters · Special protection areas · Quests · Modelling · Suspended solids · Sediments · Environmental Quality Standard · Thames Estuary marshes · Benfleet and Southend marshes

## Introduction

The Thames Estuary and Marshes special protection area (SPA) is located in the lower reaches of the estuary and includes the intertidal Mucking Flats on the north bank and the intertidal areas and marshes on the south side of the estuary from Cliffe to the Isle of Grain. On the north of the estuary the Benfleet and Southend Marshes SPA extend from Canvey Island to Shoeburyness (Fig. 1). The sites support an important assemblage of wintering waterbirds and are also important in spring and autumn migration periods.

Work by Power et al. (1999) found that copper concentrations in the Thames (collected at Erith, 26.6 km downstream of London Bridge, between 1980 and 1997) decreased over time. A study of copper distribution in the Thames Estuary for the

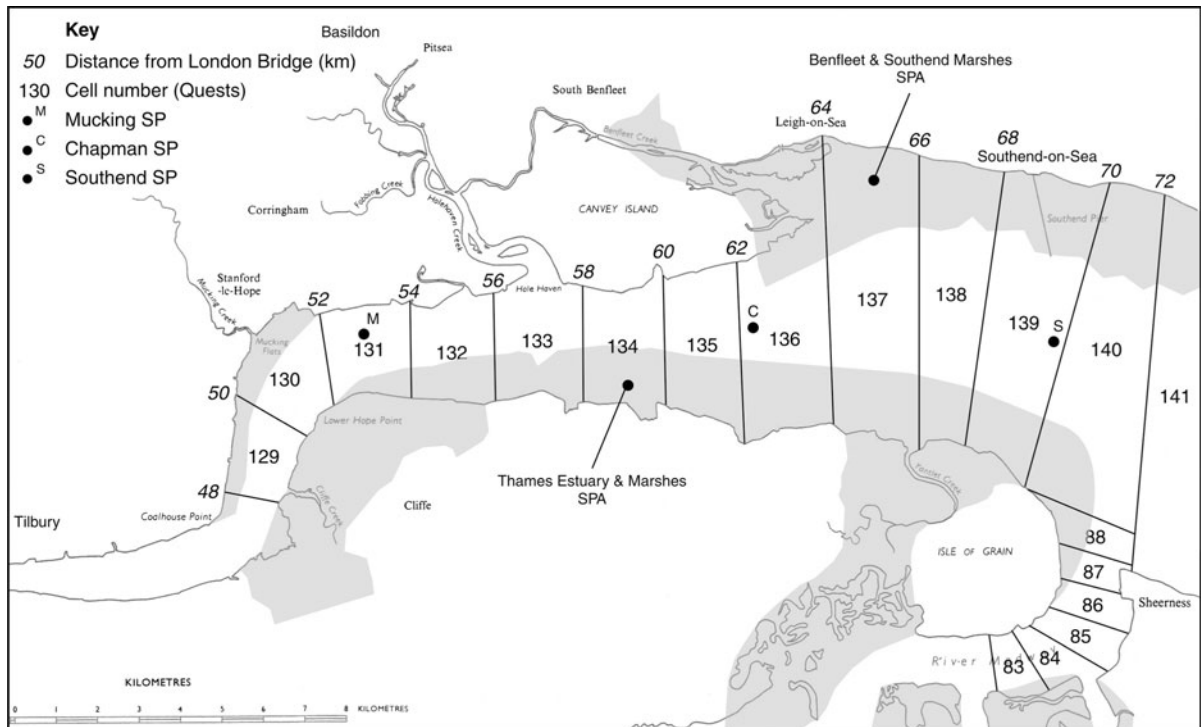
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**Fig. 1** Location of the Quests model cells and sample points (SP) in relation to the Thames Estuary and Marshes SPA and the Benfleet and Southend Marshes SPA

period 1990–1995 (Stevenson & Ng, 1999) showed the locations of the inputs and estuarine sampling sites referred to in this article and found a pattern of decreasing annual mean values of dissolved copper at most sites between 1990 and 1994. Attrill & Myles Thomes (1995) investigated copper concentrations in sediment samples and found that copper in the sediments (averaged from three sampling sessions in 1989) decreased from upper to lower estuary sites. Analysis of sediment cores by O'Reilly Wiese et al. (1997) show that copper concentrations decreased from 30 to 70% between 1944 and 1966 and this is attributed to the commissioning and updates of the sewage treatment works (STWs) at Crossness and Beckton.

During stages three and four of the Habitats Directive Review of Consents the Environment Agency (2006) investigated the water quality in the estuary to establish whether the concentrations of any substances might pose risks to the integrity of the SPAs. The investigations focussed on the role played by 11 STW consents including the major London

STWs at Beckton, Mogden, Crossness, Long Reach and Riverside.

The estuary concentrations for most metals were found to be comfortably below their Environmental Quality Standards (EQS) but there was concern in relation to copper. The perceived risk was due to the potential concentrations of copper in the STW effluents, contributing to the concentration of this metal within the estuary and giving rise to bioaccumulation within the food chain. The EQS for dissolved copper is 5 µg/l, as an annual average, and this concentration was exceeded at times during the 1990s.

This article describes studies carried out by the Environment Agency and WRC between 2005 and 2008 to examine:

- the concentrations of measured copper in the estuary and the reliability of these measurements;
- the sources of copper within the Thames catchment and the relative contributions from each, and;

- the use of modelling to help understand the relationship between input loadings and observed concentrations.

## Methods

### Concentrations of copper

A study (Murray et al., 2008) was carried out by WRc to assemble a database of all available copper data and associated factors (other metals, river flow, tide, salinity, suspended solids (SSs) and weather) at selected estuarine sites from 1995 to 2007. The aim was to use these data to explore patterns and trends in the copper data and to identify whether environmental factors can explain any of the observed patterns and trends.

Samples are routinely collected and analysed from the 12 selected sites (Table 1) along the Thames Tideway and Estuary. Methods used in the Environment Agency National Laboratory Service to analyse copper are differential pulse polarography and solid phase extraction—ICPMS (inductively coupled plasma mass spectroscopy) and are validated in accordance with accepted practice (Environment Agency, 2007). The Environment Agency carry out analysis on the unfiltered sample and record this as ‘total copper’ and on a filtered sample and record this

as ‘dissolved copper’; the difference should be a measure of the copper attached to sediments.

The Mucking, Chapman Buoy and Southend sampling sites are closest to the SPAs and their locations are shown in Fig. 1. Over the period 1995–2007 there were about 1,900 samples collected in total (from the 12 sites shown in Table 1). Initial examination of these sample data showed that a step change in copper concentrations occurred around 2000, believed to be partly related to upgrading of some STWs but also due to a change in the laboratory used for sample analysis. For this reason, the samples for the period up to and including 2001 were discarded from the subsequent data analysis. In addition, a number of individual samples were excluded where there were repeats or duplicates and where dissolved copper was greater than total copper.

This latter problem had been highlighted by the Environment Agency’s ‘Inter Determinand Validation’ (IDV) checks that showed dissolved concentrations for copper and zinc were frequently considerably greater than total concentrations. The discrepancy indicated some form of measurement error and was a serious cause for concern as it cast doubt over the integrity of the data collected.

WRc reviewed the data on total and dissolved metals (Gardner, 2007) and carried out laboratory tests for contamination during sample filtration. It was found that about 10% of copper samples from the Tideway over the period 2001–2007 had IDV failures (dissolved > total) and that the failures for about 5% of samples were >1 µg/l. Further analysis showed that the anomalous data were associated with a relatively small number of sampling occasions. The filtration tests did not reveal any significant sources of contamination and recommendations were made to improve sampling protocols and data checking.

Following this analysis, the Environment Agency carried out further data screening and WRc used the final data set of some 590 samples (about 45 per site) from the period 2002 to 2006 inclusive to provide the best summary of the copper concentrations in the estuary.

The differences between the total and dissolved copper patterns along the estuary were explored by some laboratory testing and modelling. The laboratory tests used the same analysis methods as the Environment Agency and involved the mixing and equilibration of different mixtures of estuarine water

**Table 1** Locations of routine sampling sites along the Thames Tideway and Estuary

No	Location	Distance from London Bridge (km)
1	Barnes	–17.7
2	London Bridge	0
3	Greenwich	7.7
4	Victoria Dock	11.4
5	Woolwich	14.7
6	Erith	26.6
7	Greenhithe	34.8
8	Gravesend	42.5
9	Mucking	53.2
10	Chapman Buoy	62.5
11	Southend	69.7
12	No. 2 Sea Reach	77.6

and Thames sediment and the determination of the relative proportions of copper that were associated with the particulate and dissolved phases. Tests were also carried out with deionised water. Seawater (25 l) was collected from Southsea and allowed to settle for 2 days. Portions for the tests were withdrawn from the settled sample. Filtration of each 250 ml portion of water was carried out using four filters and four syringes—to mimic the procedure reported to be adopted for field use and analysis carried out using the same methodology as the Environment Agency. The filters and bottles used were supplied by the Environment Agency from their current stocks.

The extent to which metals are absorbed onto particulate matter is described by a partition coefficient,  $K_p$ , which relates the concentration of dissolved metal in the water column to the concentration in the particulate matter and was calculated as follows:

$$K_p = C_p(\mu\text{g}/\text{kg})/C_d(\mu\text{g}/\text{l}) \quad (1)$$

$C_p$  and  $C_d$  are, respectively, the concentrations of the metal in the particulate and dissolved phases.

### Sources of copper

The next stage of work was a budget study (Kelly et al., 2008) to quantify the total copper loads being discharged to the Thames Tideway. The study sought to distinguish between:

- loads from sources upstream of the tidal limits and those being discharged directly into the Tideway; and between,
- loads discharged under dry and wet weather conditions.

### Modelling investigations

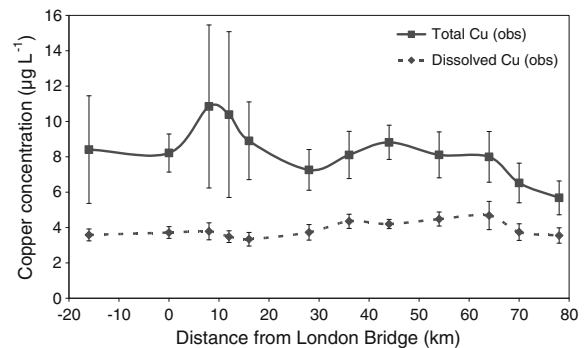
The final element of the investigations was to use the Quests Tideway estuary model to help explain the link between the source inputs and the observed concentrations of total and dissolved copper. The Quests Tideway model is a 1D hydrodynamic and water quality model originally built by WRc for the Environment Agency in the late 1980s and early 1990s. The Quests software has also been applied to the Humber Estuary by the Environment Agency as described by Wang & Cresser (2007).

## Results

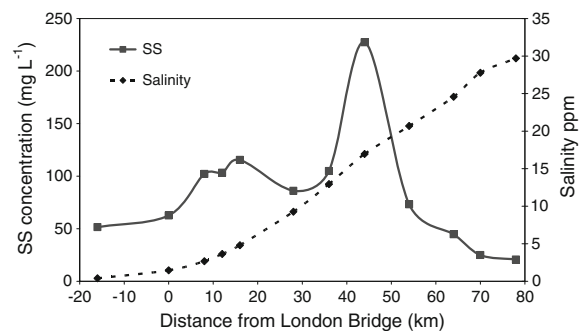
### Concentrations of copper

Figure 2 shows the mean copper concentrations for both total and dissolved copper throughout the estuary. The increase in the concentrations and variability of total copper around 10 km downstream of London Bridge is associated with inputs from the major STWs at Beckton and Crossness and from the River Lee. The subsequent increase around 30–40 km is more difficult to explain, but is likely to be linked with the increase in SSs at this location, compared to upstream and downstream sites (Fig. 3).

The pattern for dissolved copper (Fig. 2) is different from total copper in that concentrations increase in the lower estuary reaching a peak near Chapman Buoy (63 km). At this location, close to the Marshes SPAs, the mean dissolved copper is just below the 5  $\mu\text{g}/\text{l}$  EQS.



**Fig. 2** Mean total and dissolved copper concentrations 2002–2006



**Fig. 3** Mean salinity and suspended solids concentrations 2002–2006

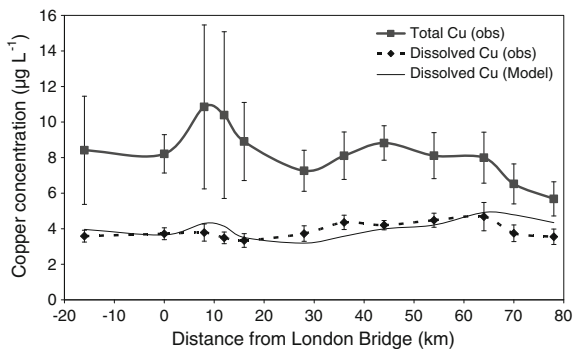
The results indicated that  $K_p$  for copper in the estuarine waters was smaller at high SS concentrations. This is typical of the so-called particle concentration effect where it is supposed that either the high concentration of particles reduces sorption by a competitive inter-particle mechanism or because the high concentrations of SS are accompanied by correspondingly increased concentrations of dissolved ligands that also might reduce sorption. Values of  $\log K_p$  in the estuarine water were found to range from 3.7 to 4.2 for low concentrations of SS (0–100 mg/l) and from 2.7 to 3.1 for higher concentrations (around 1,000 mg/l).

In addition, there was clear evidence that the  $K_p$  value for freshwater was significantly higher than for the estuarine samples. Values for  $\log K_p$  for deionised water were around 5 for low concentrations of SS and around 4 for high SS concentrations.

Combining these two effects together allowed  $K_p$  to be related to both SS and salinity. When this partitioning model was applied to the data it gave rise to a predicted dissolved copper pattern that largely explained the observed pattern (Fig. 4).

#### Sources of copper

For the Thames catchment upstream of the tidal limits (including the Medway catchment), the Environment Agency National SIMCAT model (Crabtree et al., 2009) was used to quantify river flows and STW effluent flows (Fig. 5). The model was split into a wet day model and a dry day model. Observed effluent copper data (that had been validated to exclude those with IDV failures) were used to relate copper concentrations to SS concentrations and to



**Fig. 4** Observed and modelled concentrations of dissolved copper using partitioning model

establish differential performance on wet days and dry days. These relationships were used to quantify loads from STWs without effluent copper data. The Generalised Land Use Data (DCLG, 2007) were used to quantify different land use areas by water body. Urban washoff loads were then estimated using regionally varying rainfall data and event mean concentrations by land use from literature data. Fixed wet and dry concentrations were assumed for the non-urban diffuse land use areas.

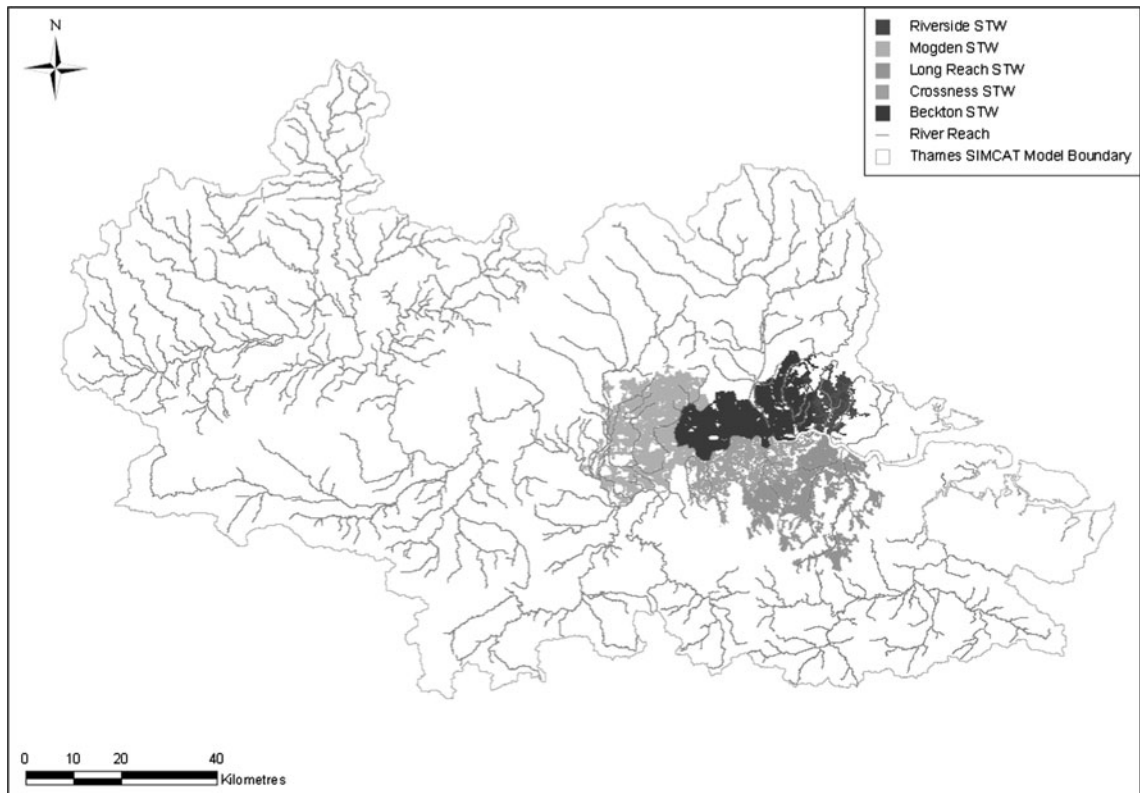
The estimated copper budget for the Thames catchment was checked by comparing the predicted loads with those observed at monitoring stations close to the tidal limits. The results (Fig. 6) show a reasonable overall agreement although loads from the Medway catchment are underestimated.

For the direct discharges to the Tideway dry weather effluent flows were based on observed data. This was extrapolated to wet day flows using rainfall driven flow modelling based on the detailed sewerage models developed by Thames Water. Wet day flows included storm tank and combined sewer overflow (CSO) discharges as well as the extra-treated flows. Observed effluent copper data were used to make best estimates of the average dry day and wet day concentrations to apply to each STW, storm tank and CSO. All of the observed data used for this exercise had been validated to exclude those with IDV failures.

The overall results of the budget exercise are summarised in Table 2. The total copper load to the Tideway was estimated to be about 36 tonnes/year with 52% of this coming from STWs. More than half of the total load was estimated to enter the Tideway on wet days. This bias towards wet day loading was largely related to the deterioration in effluent quality from the Tideway STWs and the high loading from the Tideway CSOs.

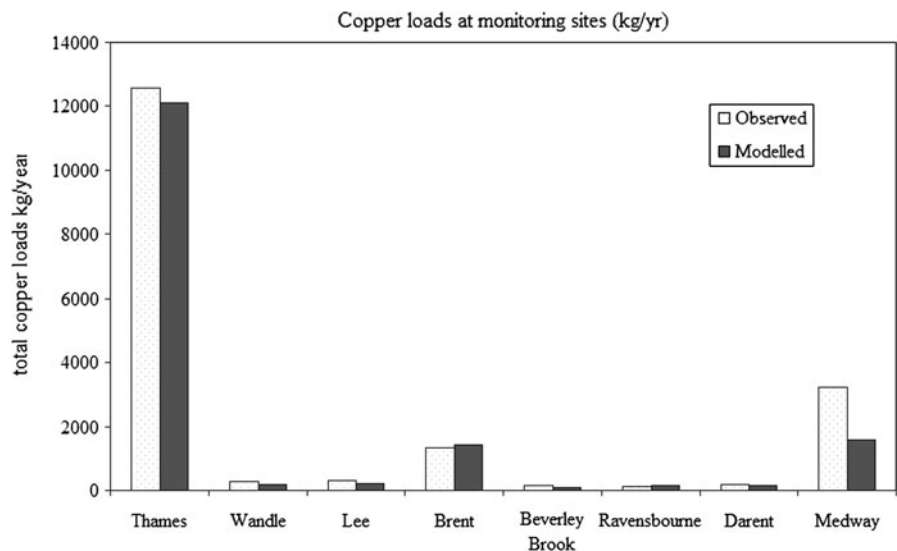
#### Modelling investigations

The Quests model includes submodels for sediments and metals. Metals are represented in two phases in the water column—dissolved and adsorbed to suspended sediments. The adsorbed metals are considered to deposit and erode in a similar fashion to the sediments onto which they are adsorbed. Within the water column, partitioning between the two phases is represented by a partitioning coefficient ( $K_p$ ) as



**Fig. 5** Thames catchment showing modelled rivers in SIMCAT and the direct Tideway urban catchments

**Fig. 6** Comparison of modelled and observed copper loads from rivers discharging to the Thames Tideway



described in Eq. 1, which varies with salinity and a rate constant.

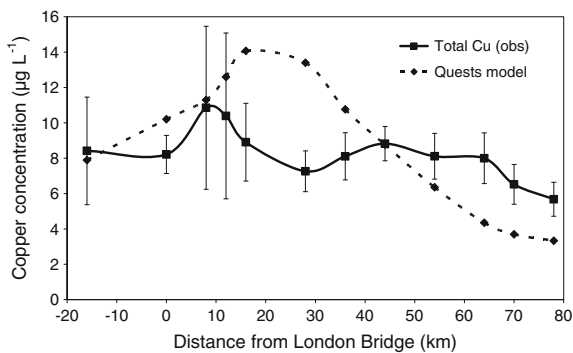
The model was used in 2005 (Chambers et al., 2005) to explore copper patterns in the estuary. The

work was updated in 2008 using the new predictions of dry and wet day loads from the sources of copper budget study. The results, in terms of total copper, are illustrated in Fig. 7 in comparison to the observed

**Table 2** Estimated copper loads to the Thames Tideway by source

Source	Dry (kg year <sup>-1</sup> ) <sup>a</sup>	Wet (kg year <sup>-1</sup> ) <sup>a</sup>	Total (kg year <sup>-1</sup> )	% Total inputs
Upstream of tidal limits				
Non-urban diffuse	6,600	1,700	8,300	21
STW discharges	4,300	2,200	6,500	16
Industrial discharges	800	500	1,300	3
Urban washoff	0	4,800	4,800	12
Total inputs	11,700	9,200	20,900	
Load removed by abstractions	-2,700	-1,100	-3,900	-
Total (net abstractions)			17,100	
Direct discharges				
Major STWs	4,800	7,200	12,000	31
Storm tanks	0	300	300	1
Other STWs	900	1,000	2,000	5
CSOs	0	4,400	4,400	11
Total inputs	5,700	12,900	18,700	
All STWs	10,000	10,400	20,500	52
Grand total inputs	17,400	22,100	39,600	
Grand total (net abstractions)			35,700	

<sup>a</sup> Assumes 20% days wet, 80% days dry. Numbers rounded to nearest 100 kg year<sup>-1</sup>

**Fig. 7** Observed (2002–2006) and modelled mean total copper concentrations

copper concentrations. The model overpredicts the total copper concentrations in the middle Tideway and in the lower Tideway the model fails to reproduce the increase in copper concentrations observed around 40–50 km. The comparison between the model and observed data for dissolved copper concentrations follow a similar pattern to that described for total copper.

Despite the limitations in the Quests model, simulations (for a year of tidal cycles), were carried out to provide an indication of the reduction in dissolved copper concentrations that would be expected following the fourth Water Industry Asset Management Programme (AMP4) upgrading of the

Tideway STWs. It was assumed that there would be reductions in suspended sediment and attached copper loads discharged from the Beckton, Crossness, Mogden, Long Reach and Riverside STWs. The results (Fig. 8) indicate that a reduction of about 1 µg/l in the middle Tideway, reducing to about 0.5 µg/l near the Thames Estuary and Marshes SPA and Benfleet and Southend Marshes SPA, could occur.

## Discussion

### Concentrations of copper

The ‘turbidity maximum’ where observed SS is at a maximum at a mid-point between fresh and estuarine waters is a common phenomenon in many estuaries and is thought to result from the interaction of two transport processes—the landward transport of sediment from the sea and the trapping of sediment from rivers and other sources within the system (Uncles & Mitchell, 2011). It is often associated with the remobilisation of bed sediment which can release absorbed metal into the water column. After 40 km (near Gravesend), total copper concentrations decline into the lower estuary.

The observations made in the Tideway can be used to relate the total and dissolved copper concentrations to the SS turbidity maximum using the  $K_p$  value. It would be expected that higher  $K_p$  values and total copper values occur when salinity is lower and SS is higher in the mixing zone for fresh and estuarine waters. This gives rise to a ‘copper maximum’ phenomenon at the optimum salinity and SS concentrations mirroring the turbidity maximum.

### Sources of copper

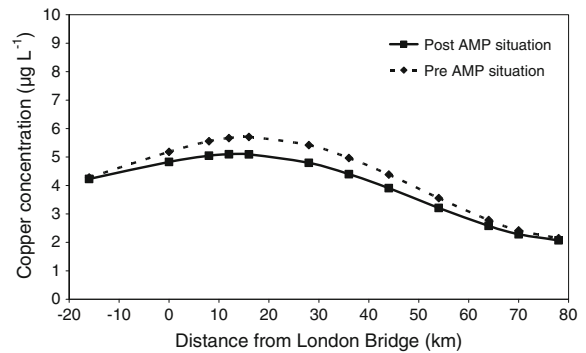
The match to observed copper at the end of the catchments entering the Tideway indicates that the sources have been well estimated. The underestimate of loads from the Medway catchment possibly indicate a missing source. The uncertainty around the sources of copper results were not quantified in the study and is likely to be more significant for the non-urban diffuse and urban washoff sources than for the point sources. A source of copper not accounted for in the budget is that accumulated in historic sediments that could be exposed by dredging operations and erosion (O’Reilly Wiese et al., 1997).

The budget shows that the emphasis on managing copper is rightly focussed on the point source from the STWs (52% load) but diffuse sources such as wet weather urban runoff (12% load) could also be managed to reduce the load to the Tideway.

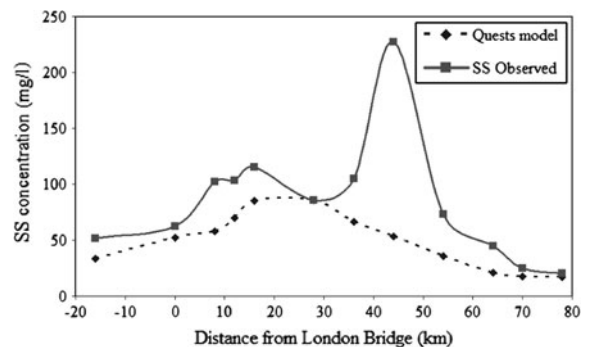
### Modelling investigations

The overprediction of total copper concentration in the middle Tideway suggests that the input loads calculated for the major treatment works at Beckton and Crossness may be overestimated. The underprediction of the observed increase in copper concentrations around 40–50 km is linked to the fact that the model does not generate the peak in SS concentrations at this location (Fig. 9). The Quests model has subsequently been enhanced to better represent turbidity maxima in estuaries, but this has not yet been applied to copper predictions in the Thames Tideway.

The Quests model also struggled to replicate the observed pattern in dissolved copper concentrations. This was mainly because of the mismatch for the total copper predictions but also because the model currently only allows the partition coefficient to vary



**Fig. 8** Predicted change in dissolved copper concentrations as a result of the AMP4 STW upgrading



**Fig. 9** Observed (2002–2006) and modelled mean suspended solids concentrations

with salinity and not with SS. The earlier laboratory work identified that  $K_p$  values were affected by SS concentrations and this is a further enhancement required in the model.

The simulations showed the predicted improvement in copper concentrations as a result of upgrading the main London STWs during the AMP4 investment period. This has increased the Environment Agency’s confidence in meeting the EQS requirements for the SPAs in the future (Fig. 8).

### Conclusions

The copper studies carried out by the Environment Agency and WRc for the purpose of managing the Thames Estuary and Marshes SPA and the Benfleet and Southend Marshes SPA have helped in a number of respects, namely to improve confidence in the sampling data and increase understanding about the



observed patterns in total and dissolved copper along the estuary in relation to inputs and partitioning processes. The work has given a preliminary quantification of ‘current’ sources of copper loads which helps to confirm the relative significance of different sources and to identify where uncertainties are greatest. The modelling work has clarified the key sediment and partitioning processes that need to be incorporated in the estuary models for these models to produce reliable predictions. The work also highlights the increasingly important role of modelling in the development of water quality policy and management of the water environment, which will be of benefit to both the regulator and dischargers.

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