SPATIAL AND VERTICAL DISTRIBUTION OF ESTROGENIC ACTIVITY IN RIVER BED SEDIMENTS.

Kerry Evans, Sam Valbonesi, Edwina McKechnie, Andy Cundy & Elizabeth Hill

Centre for Environmental Research, School of Life Sciences, Chichester Building, University of Sussex, Falmer, Brighton, BN1 9QJ. Email: K.L.Evans@sussex.ac.uk

Abstract

To establish the distribution of estrogenic contaminants in river-bed sediments, samples were collected downstream of several Wastewater Treatment Works (WwTWs) on the River Ouse, Sussex, UK. Sediments were extracted and analysed for total estrogenic activity in a recombinant yeast estrogen screen assay. Estrogenic activity was calculated as ng estradiol equivalents/kg dry weight of sediment (ng E2eq/kg). The top 1cm of the bed sediments contained low concentrations of estrogenic activity (<80ng E2eq/kg) at sites below major WwTWs effluents (population equivalents, PE, 37,045) entering the main course of the river. However, highest sediment concentrations of estrogenic activity (>2000 ng E2eq/kg) were observed at sites below minor WwTWs (PE 1500) discharging into small tributaries. The levels of total estrogenicity in sediments downstream of WwTWs declined with increasing distance from the source and reflected the predicted overlying water concentrations of estrogens derived from the GREAT-ER model. Analysis of estrogenic activity in sediments in the tidal reaches revealed significant intra-site spatial variability with typical values of 1802 $\pm$ s.d. 2686 and 515 $\pm$ 426 ngE2eq/kg. To examine the vertical distribution of estrogens at contaminated sites, sediments were cored, sectioned and dated radiometrically. The highest concentrations of estrogenic activity were detected in the top 5cm of the cores in sediments <100days old (1000-5000 ngE2eq/kg at contaminated sites). In sediments greater than >100 days old, estrogenic activities were between 600-5000 ngE2eq/kg. In the deeper bed clays (13-33 cm depth) sediment concentrations declined significantly, but remained above the limits of detection (30 ngE2eq/kg). This study suggests appreciable aquatic contamination with estrogens can arise from inputs of low levels of WwTW discharges into river catchments, and that estrogens persist in older buried sediments, with the possibility of vertical migration of these contaminants through the bed clays.

Introduction

• Estrogens present in WwTW final effluents are known to associate with bed sediments. Recent work (Peck *et al*, 2004) has shown that in the River Ouse the majority of these compounds are in the form of estradiol and estrone.

•The aim of this study was to determine the distribution of estrogens in the Ouse catchment and to investigate the depth profile of these compounds.

•Levels of estrogens in water were predicted using the GREAT-ER model (Geo-Referenced Exposure Assessment Tool-European Rivers) and thus sites with highest estrogen prediction levels were selected to analyse the estrogenic activity in the top few centimetres of the sediments.

• To determine the fate of estrogens in buried sediments a few of the sites which showed elevated levels of estrogenic activity in the surface sediments were selected for coring and further analysis.

Materials & Methods

• 10 sites were selected to investigate levels of estrogens in the surface sediments. Estrogens in sediments were extracted using Microwave-Assisted Solvent Extraction (MASE) using method developed by Liu *et al* 2004. Extracts were then purified using Oasis polymeric Solid Phase Extraction (SPE) Cartridges (Waters).

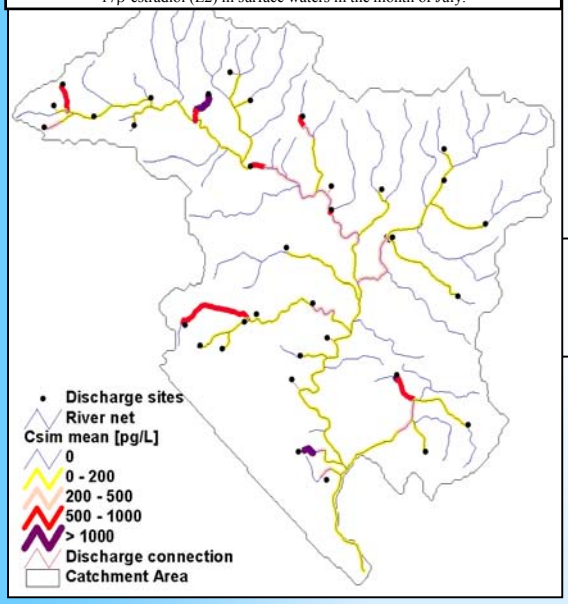
• SPE extracts were then analysed in a recombinant yeast transcription assay to determine estrogenic activity. In the yeast estrogen screen (YES) assay, extracts are compared to the natural ligand of the receptor (17β-estradiol) to establish the estrogenic activity in terms of equivalence.

• Sites demonstrating elevated levels of estrogenic activity were selected for study of buried sediments (maximum depth of 40cm). Sediments were cored, sectioned and dated radiometrically using a gamma spectrophotometer.

• Sediments were also analysed for particle size and total organic carbon (TOC) content.

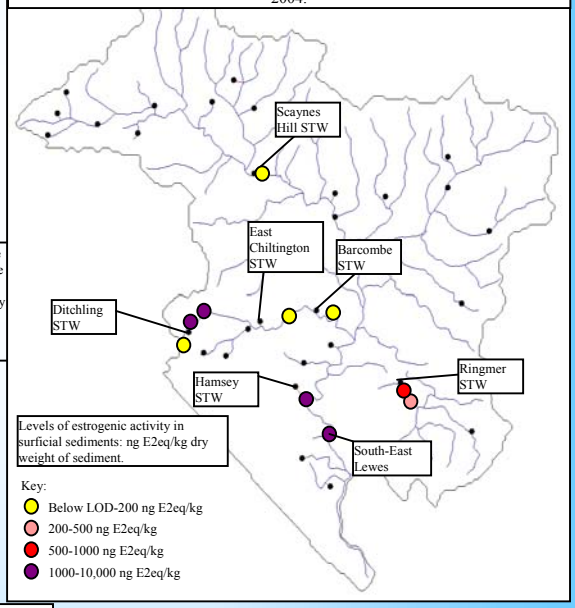
Results and Discussions

Figure 1: GREAT-ER model of the River Ouse Catchment predicting levels of 17β-estradiol (E2) in surface waters in the month of July.



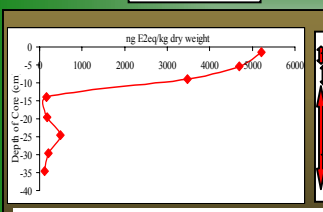
Levels of estrogens in surface sediments (figure 2) reflect the relative concentrations of the overlying water as predicted by the GREAT-ER model simulation for the steroidal estrogen (E2) (figure 1).

Figure 2: Map of estrogenic activity of surface sediments in samples collected July, 2004.



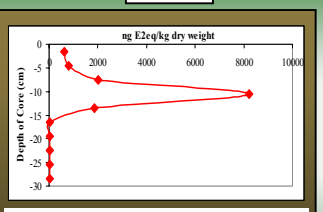
Sediment Core Profiles

South East Lewes



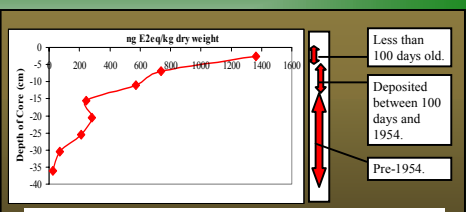
Estrogen concentrations in sediments in the South East Lewes core are high at the top of the core (up to a depth of 11cm) dated as being more than 100days old but less than 50 years in age. Concentrations then decline rapidly with depth. When plotted against TOC the same trends are revealed. Particle size is consistent throughout the length of the core.

Ditchling



Estrogen concentrations in sediments in the Ditchling core are greatest at a depth of 10cm. Concentrations then decline rapidly with depth. When plotted against TOC the same trends are revealed. Particle size is consistent throughout the length of the core.

Hamsey



Estrogen concentrations in sediments in the Hamsey core are high at the top of the core (up to a depth of 13cm) dated as being more than 100days old but less than 50 years in age. Concentrations then decline rapidly with depth. When plotted against TOC the same trends are revealed. Particle size is consistent throughout the length of the core.

Conclusions

• The pattern of concentrations of estrogens in surface sediments reflected those predicted for the overlying surface water concentrations from the GREAT-ER model.

• Levels of estrogens declined with depth but significant concentrations remained in sediments that had been buried for more than 100 days.

• This suggests that either estrogens are mobile and leach down into the buried sediments or that they are highly persistent in buried sediments. The nature, leaching and persistence of these estrogens in these sediments are currently being investigated.

References

Liu, R., Zhou, J.L. & Wilding, A. (2004) Microwave-assisted extraction followed by gas chromatography-mass spectrometry for the determination of endocrine disrupting chemicals in river sediments — *Journal of Chromatography A*, **1038**, 19-26.

Peck, M., Gibson, R.W., Kortenkamp, A. & Hill, E. M. (2004) Sediments are Major Sinks of Steroidal Estrogens in Two United Kingdom Rivers — *Environmental Toxicology and Chemistry*, **23**, 945-952.

Acknowledgements

Research is funded by a grant from the EU ERDF Programme, Interreg III and an undergraduate Nuffield bursary to S.V.

Yeast cell cultures (YES & YAS) were kindly provided by Professor John Sumpter, Brunel University, UK.