



# Improved removal of estrogenic and pharmaceutical compounds in sewage effluent by full scale granular activated carbon: Impact on receiving river water

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## ARTICLE INFO

### Article history:

Received 8 June 2010

Received in revised form

23 September 2010

Accepted 1 October 2010

Available online 28 October 2010

### Keywords:

Endocrine disrupting chemicals

Steroidal estrogens

Pharmaceuticals

Sewage effluents

Liquid chromatography–tandem mass

spectrometry

Granular activated carbon

## ABSTRACT

Sewage effluents are widely recognised as the main source of emerging contaminants, such as endocrine disrupting chemicals (EDCs) and pharmaceuticals in surface waters. A full-scale granular activated carbon (GAC) plant has been installed as an advanced technology for the removal of these contaminants, in a major sewage treatment works (STW) in South-West England as part of the UK National Demonstration Programme for EDCs. This study presented for the first time, an assessment of the impact of a recently commissioned, post-tertiary GAC plant in the removal of emerging contaminants in a working STW. Through regular sampling followed by solid-phase extraction and analysis by liquid chromatography–tandem mass spectrometry (LC–MS/MS), a significant reduction in the concentrations of steroidal estrogens was observed (>43–64%). In addition, significant reductions were observed for many of the pharmaceutical compounds such as mebeverine (84–99%), although the reduction was less dramatic for some of the more widely used pharmaceuticals analysed, including carbamazepine and propranolol (17–23%).

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## 1. Introduction

Research on water pollution from emerging contaminants such as endocrine disrupting chemicals (EDCs), pharmaceuticals and personal care products (PPCPs) is one of the important aspects of current environmental research due to their potential toxic effects on wildlife and humans [1–3]. EDCs are of global concern and broadly defined as chemicals that may interfere with the function of the endocrine systems in wildlife and humans. Endocrine disruption has been shown to reduce fish fertility, to be linked to human cancers and may also affect human fertility [4]. A wide range of compounds has been found to possess, or are suspected of possessing, endocrine disrupting properties. Many pharmaceuticals and EDCs are classified as priority substances in the EU Water Framework Directive (2000/60/EC). Due to their potency, the steroidal estrogens, such as the natural estrone (E1) and 17 $\beta$ -estradiol (E2), and the synthetic 17 $\alpha$ -ethinylestradiol (EE2) are of greatest concern and have been found to exhibit feminising effects on fish at very low concentrations (e.g. 1 ng L<sup>-1</sup>) [5,6]. PPCPs are also of widespread concern due to their ubiquity in the aquatic environment, as a result of their increased use and number, and their

potential for deleterious effects to wildlife, which to date is largely unknown [7].

The majority of EDCs and PPCPs are man-made, organic chemicals being introduced to the environment by anthropogenic inputs, e.g. EE2 is the main component of the oral contraceptive pill, and carbamazepine and diclofenac are, respectively, used as anti-epileptic and anti-inflammatory drugs. In addition, EDCs can be naturally occurring in the environment, e.g. the female hormones E1 and E2 are both excreted by females and are hence ubiquitous in the aquatic environment. Such compounds may not be removed by sewage treatment works (STW) and may even be reactivated through deconjugation during these processes [8–10], hence prolonging their residence in the aquatic environment. Steroidal estrogens and some PPCPs have been found to persist through many sewage treatment processes [8–12], and it is widely recognised that effluent discharges from STW are the main source of EDC and PPCPs inputs to the aquatic environment, such as rivers and streams [8,13–15]. Although the concentrations of steroidal EDCs are generally low in aquatic systems, concentrations of up to 19.4 ng L<sup>-1</sup> have been detected in surface waters and levels as high as 5400 ng L<sup>-1</sup> have been found in some STW effluents [11].

Due to increasing concerns for the implications for fish populations and human health and the identification of sewage effluents as the major point source, a research focus in recent years has been on the identification of suitable technologies which satisfac-

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**Table 1**  
Physicochemical properties of the pharmaceuticals and their analysis conditions.

Compound	Therapeutic class	Molecular mass	log $K_{ow}$	pK $_a$	Ionisation mode	RT (min)	Collision energy (eV)	Precursor ion (m/z)	Product ion (m/z)
Propranolol	Anti-hypertensive	259	1.2–3.48	9.5	ES+	9.95	20	260	116 (100%), 183 (56%)
Sulfamethoxazole	Antibiotic	253	0.5	2.0 or 5.5	ES+	11.2	15	254	92 (100%), 108 (65%), 156 (16%)
Mebeverine	Gastrointestinal	429		8.1	ES+	12.2	25	430	101 (100%), 135 (3%)
Thioridazine	Anti-depressant	370		9.5	ES+	14.3	25	371	126 (100%), 98 (75%)
Carbamazepine	Anti-epileptic	236	2.45	13.9	ES+	14.8	20	237	194 (100%)
Tamoxifen	Anti-cancer	371	6.3		ES+	16.8	25	372	72 (100%), 208 (1%)
Mecoprop	Herbicide	214			ES–	19.7	20	213	141 (100%)
Indomethacine	Analgesic/antipyretic	357	4.27	4.5	ES+	22.0	25	358	139 (100%), 141 (20%)
Diclofenac	Anti-inflammatory	295	4.5	4.15	ES+	22.1	30	296	214 (100%)
Meclofenamic acid	Anti-inflammatory	295	5.12	4.2	ES+	24.1	25	296	243 (100%)
Monensin	Growth promoters	692	2.75–3.89	6.65	ES+	28.7	40	693	676 (100%)

torily remove emerging contaminants, from wastewater. Granular activated carbon (GAC), albeit expensive, has long been used in the removal of traditional organic contaminants such as pesticides [10]. GAC has therefore been proposed as a potential treatment method to aid in the effective removal of emerging contaminants, particularly EDCs in wastewater treatment [16], although up to now the majority of these investigations have been laboratory-based [17,18]. This study aimed to assess the removal efficacy for several emerging contaminants by a recently commissioned, post-tertiary GAC plant, through the regular sampling and analysis of effluent samples before GAC installation (pre-GAC) and after GAC installation (post-GAC). The concentrations of the selected steroidal estrogens and pharmaceutical compounds have also been analysed at three downstream locations and an upstream location in the receiving river, and a control site from another local river, over a 3-year period, to allow a full evaluation of the impact of GAC on the quality of water downstream of sewage effluent discharge.

## 2. Experimental

### 2.1. Chemicals and standard solution

All of the solvents used, including methanol and acetonitrile, were purchased from Rathburn Chemicals Ltd., Walkersburn, UK, and were of distilled-in-glass grade. Authentic chemical standards including E1, E2 and EE2, propranolol, sulfamethoxazole, mebeverine, thioridazine, carbamazepine, tamoxifen, mecoprop, indomethacine, diclofenac, meclofenamic acid and monensin were purchased from Sigma, Dorset, UK. The pharmaceutical compounds were chosen as they represent different therapeutic classes, are widely used in the UK, and have different physicochemical properties (Table 1). Deuterated internal standards, E2-d<sub>2</sub>, E2-d<sub>4</sub>, EE2-d<sub>4</sub> and E1-d<sub>4</sub> were also purchased from Sigma, Dorset, UK. Diuron-d<sub>6</sub> and <sup>13</sup>C-phenacetin were purchased from Cambridge Isotope Laboratories, Andover, USA. All standards were prepared in methanol and were stored at –18 °C. Formic acid was of HPLC grade. Ultrapure water was supplied by a Maxima Unit from USF Elga, Marlow, UK.

### 2.2. The STW

The full setup of the STW at Swindon, UK, studied in this work is shown in Fig. 1a, which serves a population of approximately 155,000. It consists of primary and secondary activated sludge treatment. Briefly, the raw sewage was passed through screens to remove or reduce the size of trash and large solids that get into the sewage system, with the solids collected and scraped off for disposal. The sewage was then further treated in primary settlement tanks for removing both settleable and floatable solids, a process that is often aided by the addition of flocculants. To remove biochemical oxygen demand, the wastewater was further treated by

an activated sludge process, which is a well established secondary treatment process. Finally, the wastewater was further treated in final settlement tanks before discharge to the River Ray. The organic content of secondary effluent had been measured, this varying from 1 to 3.3 mg L<sup>-1</sup> for 5-day biochemical oxygen demand (BOD<sub>5</sub>) and from 11 to 27 mg L<sup>-1</sup> for chemical oxygen demand (COD).

To improve effluent quality and as part of the high profile National EDC Demonstration Programme (NDP) of the UK, a GAC plant (Fig. 1b) was proposed at the STW to extend the existing conventional treatment line, which has been shown to be inefficient in the removal of both EDCs and pharmaceutical compounds [12,19,20]. The NDP had been undertaken by all 10 water companies in England and Wales and is being coordinated by UK Water Industry Research. The NDP consists of two phases: the investigation of EDC removal by a wide range of conventional sewage treatment processes through extensive monitoring at 14 STWs; and the investigation of advanced treatment processes aimed at achieving very high standards of EDC removal. The key objective of the GAC project, supported by the UK Environment Agency, was to demonstrate the impact of full scale GAC treatment on the aquatic life of the Ray River which is receiving the treated effluent from the STW. The construction of the GAC plant began in 2007, with GAC filling in November 2007. It was fully commissioned in March 2008. In total, 1900 m<sup>3</sup> of GAC supplied from Norit (Glasgow, UK) was used in this application. The GAC used had the following properties: 0.50 g mL<sup>-1</sup> apparent density, 1.0 mm effective size, 920 mg g<sup>-1</sup> iodine number.

### 2.3. Sampling and sample treatment

To ensure good quality assurance, all sampling was conducted in triplicate. As the source of EDCs and pharmaceuticals to rivers, effluent samples from the STW were taken seasonally between April 2006 and November 2008, using pre-cleaned glass bottles (2.5 L) or stainless steel barrels (50 L) with the aid of an automated pumping system developed by the authors, set to collect samples at 4-h intervals. Altogether 45 effluent samples were taken. Due to site restrictions from the water company concerned on health and safety grounds, influent samples could not have been taken. It is therefore the limitation of this work that a direct comparison between influent and effluent samples could not be made.

River samples were collected in triplicate, from the receiving river Ray, in pre-cleaned Winchester amber-glass bottles (2.5 L), approximately 3.5 km upstream and 10 m, 1.7 km and 8.3 km downstream of the STW effluent, and at a control site on the river Ock (due to its high water quality with no sewage inputs), over the three-year period encompassing periods both before and after GAC commission (Table 2). These sites were selected as required by the mathematical model EXAMS (exposure analysis modelling system) to be used for simulating the concentrations of EDCs in the catchment. In total, 132 samples of river water

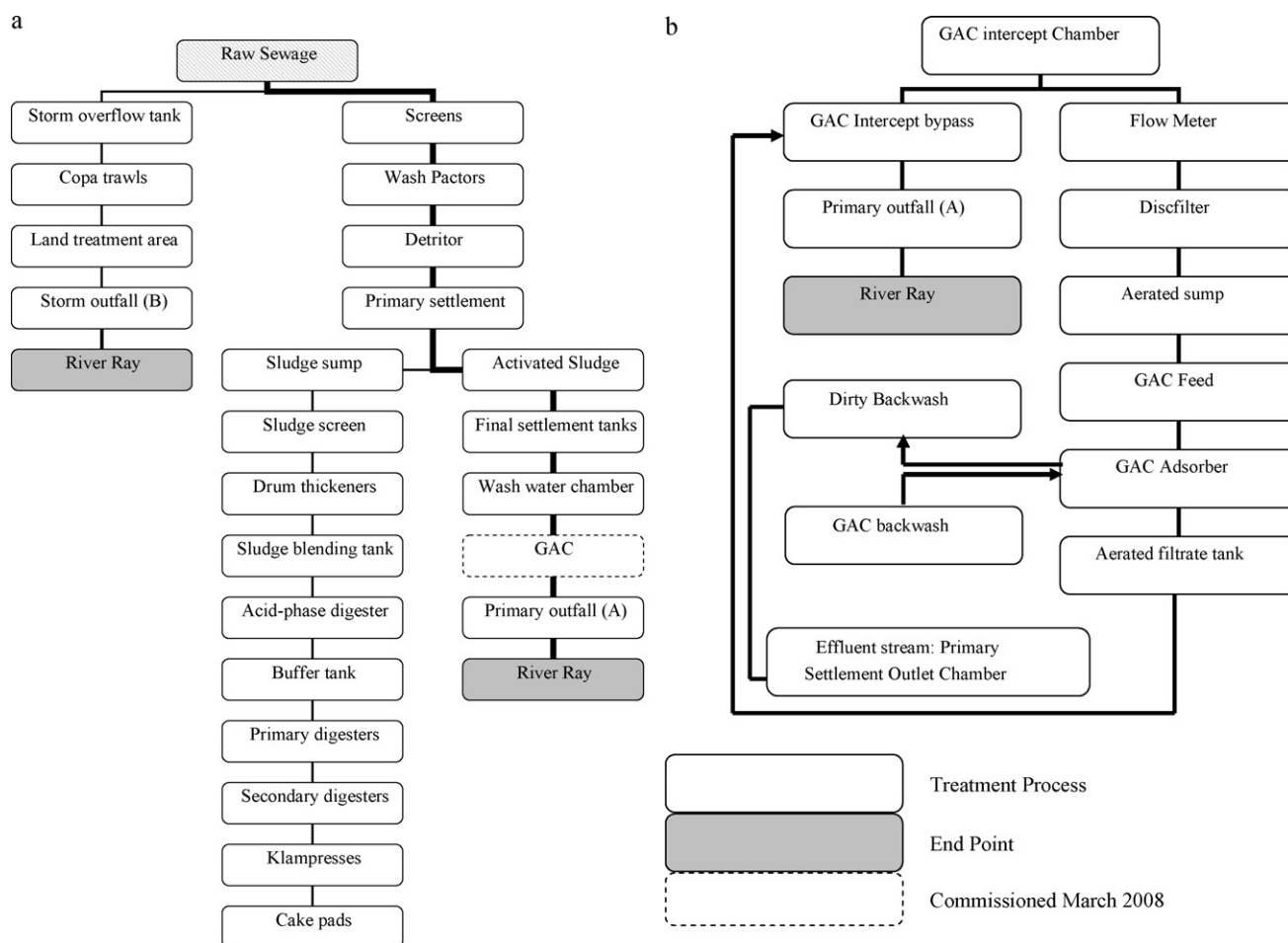


Fig. 1. The flow chart of: (a) the STW plant and (b) the GAC plant being investigated by this study.

were taken. Once sampled, sodium azide ( $5 \text{ mL}^{-1}$ ,  $2 \text{ M}$ ) was added to all samples as a general biocide to eliminate bacteria and thus minimise biodegradation during sample storage and processing. Samples were refrigerated at  $4^\circ\text{C}$  before filtration and extraction within 1 week of sampling. Samples were processed following previously published methods [21–24]. Briefly, samples were filtered under vacuum using pre-ashed glass fibre filters (GF/F,  $0.7 \mu\text{m}$  pore size) from Whatman (Brentford, UK). Filtered samples ( $2 \text{ L}$ ) in triplicate were all spiked with the internal standards ( $100 \text{ ng}$ ).

#### 2.4. Solid phase extraction (SPE)

The target compounds were extracted from the filtered water samples using SPE. The Oasis SPE cartridges ( $0.2 \text{ g HLB}$ ) from Waters (Milford, USA) were conditioned with  $5 \text{ mL}$  of ethyl acetate to remove residual bonding agents, followed by  $10 \text{ mL}$  of methanol which was drawn through the cartridges under a low vacuum to ensure that the sorbents were soaked in methanol for  $5 \text{ min}$ . Ultrapure water ( $3 \times 5 \text{ mL}$ ) was then passed through the cartridges at  $1\text{--}2 \text{ mL min}^{-1}$ . Water samples were then extracted at approx-

Table 2  
River sampling dates over the 3-year period with mean water properties for each month.

Year	GAC status	Month	pH	Temperature ( $^\circ\text{C}$ )	Dissolved oxygen ( $\text{mg L}^{-1}$ )	Conductivity ( $\mu\text{S cm}^{-1}$ )
2006	Pre-GAC	April	7.6	15.7	7.2	1024
		June	7.5	16.1	7.1	1033
		August	7.7	16.6	7.3	1053
		October	7.8	17.2	8.0	1058
2007	Pre-GAC	April	7.6	14.6	8.6	1063
		June	7.8	17.3	6.9	1059
		September	7.7	16.8	7.2	1061
2008	Post-GAC	May	7.4	16.6	7.1	870
		July	7.6	16.1	7.3	874
		September	7.3	15.8	7.1	888
		November	7.2	16.2	7.7	892

imately  $10 \text{ mL min}^{-1}$  as this has been shown to be the optimum condition for recovering the target compounds from water samples [22]. The SPE cartridges were subsequently dried under vacuum and the extracts eluted from the sorbents into 20 mL vials with 10 mL of methanol at a flow rate of  $1 \text{ mL min}^{-1}$ . The solvent was then blown down to  $100 \mu\text{L}$  under a gentle  $\text{N}_2$  flow and ready for analysis.

### 2.5. Sample analyses by LC–MS/MS

The LC separation was conducted with a Waters 2695 HPLC separations module (Milford, MA, USA) fitted with a Waters Symmetry  $\text{C}_{18}$  column ( $2.1 \text{ mm} \times 100 \text{ mm}$ , particle size  $3.5 \mu\text{m}$ ). The LC–MS/MS method used here was discussed briefly, by implementing previously developed methods [23,25]. The mobile phase comprised eluent A (0.1% formic acid in ultrapure water), eluent B (acetonitrile) and eluent C (methanol) being run at a flow rate of  $0.2 \text{ mL min}^{-1}$ . The elution started with 10% of eluent B, followed by a 25 min gradient to 80% of eluent B and a 3 min gradient to 100% of eluent B, and then changed to 100% of eluent C within 8 min, held for 10 min and then returned back to the initial conditions within 4 min. The system re-equilibration time was 10 min and the sample injection volume was  $10 \mu\text{L}$ . The MS/MS analyses were completed with a Micromass Quattro triple–quadrupole mass spectrometer equipped with a Z-spray electrospray interface. The analyses for steroidal estrogens and mecoprop were done in the negative ion mode; analysis for all of the other pharmaceutical compounds was performed in positive ion mode. The electrospray source block and desolvation temperature were 100 and  $300^\circ\text{C}$ , respectively; capillary and cone voltages were 3.0 kV and 30 V, respectively; argon collision gas  $3.6 \times 10^{-3} \text{ mbar}$ ; cone nitrogen gas flow and desolvation gas: 25 and  $550 \text{ L h}^{-1}$ . The mass spectrometer was operated in multiple reaction monitoring (MRM) mode with unit mass resolution on both mass analysers.

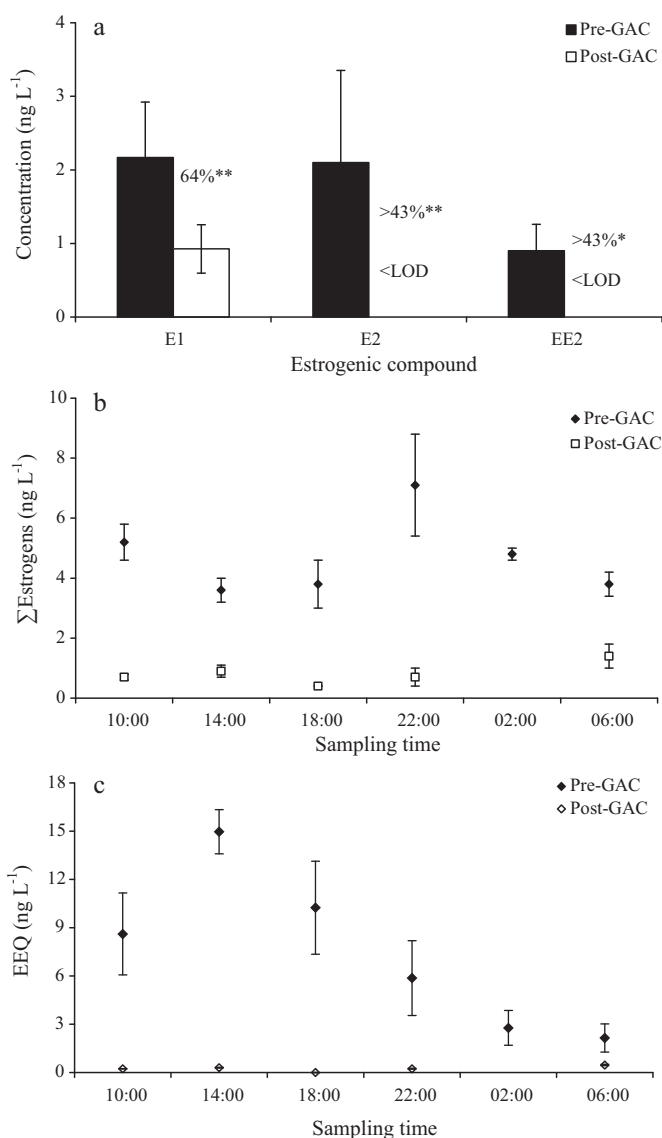
## 3. Results and discussion

### 3.1. Concentration of EDCs in STW effluent

As the source of inputs for EDCs and PPCPs in the river systems, the STW effluent was the focus of this research in terms of sampling and analysis. Initial observations during the filtration of post-GAC effluent water showed a significant reduction in the amount of suspended particulate matter in samples. This was subsequently quantified and a  $\sim 10$ -fold reduction was observed in all effluent samples (mean pre-GAC of  $0.05 \text{ g L}^{-1}$  compared with a mean post-GAC of  $0.006 \text{ g L}^{-1}$ ).

From the measurement of EDC concentration in the effluent samples, it is clear that a significant reduction in the concentrations of E1, E2 and EE2 in effluent samples was observed. Prior to GAC installation, the measured concentration range for each compound was  $0.6\text{--}3.1 \text{ ng L}^{-1}$ ,  $<1.2\text{--}5.4 \text{ ng L}^{-1}$  and  $<0.4\text{--}1.7 \text{ ng L}^{-1}$  for E1, E2 and EE2, respectively. After GAC installation, the measured concentration range for E1 fell to  $<0.6\text{--}2.0 \text{ ng L}^{-1}$ . Concentrations of E2 and EE2 were below the method limit of detection (LOD) of  $1.2 \text{ ng L}^{-1}$  and  $0.4 \text{ ng L}^{-1}$ , respectively, in all samples.

The mean concentrations of EDCs in the effluents before and after GAC are shown in Fig. 2a, where a reduction of 64% for E1, and at least 43% for E2 and EE2 was observed. When estrogen concentration was not detected, their respective LOD value was used in calculating the percentage of removal, hence such calculations were of a conservative estimate. The results suggest a major improvement in the removal of EDCs from sewage effluent with the GAC plant. It is important to note that such reduction estimates of EDC concentrations were based on a comparison of pre-



**Fig. 2.** Comparison of the pre- and post-GAC effluent samples for: (a) mean concentrations of steroidal estrogens, (b) temporal variability of measured total steroidal estrogens, and (c) temporal variation of estrogenic activity represented by EEQ. Error bar = one standard deviation. Symbols \*\* and \* represent  $P$  values of  $<0.01$  and  $<0.05$ , respectively.

and post-GAC effluent samples only, rather than a direct comparison of influent and effluent samples in each case. As a result, the other factors affecting the influent and hence effluent quality, such as chemical composition of influent during the study period, were not explicitly considered. Based on available data (e.g. Table 2), the only significant change in the STW during 2006 and 2008 was the introduction of GAC, it is therefore reasonable to attribute reductions in EDC concentrations to the operation of GAC, although the uncertainty involved in the estimation was acknowledged.

The EDC concentrations changed with time during the 24-h periods, as shown in Fig. 2b. The total EDC concentrations ( $\text{E1} + \text{E2} + \text{EE2}$ ) ranged from  $3.6 \text{ ng L}^{-1}$  at 14:00 to  $7.1 \text{ ng L}^{-1}$  at 22:00, suggesting increased discharge of estrogenic compounds at the end of a working day before GAC was installed. Following GAC installation, the variability of EDC concentrations was less obvious (relative standard deviation (RSD) = 17% for E1, and 0% for both E2 and EE2), primarily because most of the EDCs had been removed by the improved GAC technology.

In assessing the environmental impact of EDCs, often their estrogenic potency is a key parameter, as different chemicals can cause biological effects (e.g. fish feminisation) at different concentrations. To factor this difference in potency into consideration, the so-called E2 equivalence (EEQ), was calculated as follows [26]:

$$EEQ = C_{E2} + \frac{1}{3}C_{E1} + 10C_{EE2} \quad (1)$$

where  $C_{E2}$ ,  $C_{E1}$ , and  $C_{EE2}$  represent the concentrations of E2, E1 and EE2, respectively.

As shown in Fig. 2c, EEQ concentrations varied from 2.2 to 14.6 ng L<sup>-1</sup> before GAC, with the maximum value being detected at 14:00 which is primarily due to the highest EE2 concentration (1.3 ng L<sup>-1</sup>) then. It is expected that there would be a time lag between the use of EE2 (as the main component of oral contraceptive pills) and the time it was found in sewage effluent, due to transport and residence in sewerage and sewage systems. Following GAC treatment, the EEQ values were reduced to ≤0.5 ng L<sup>-1</sup>. Such major reductions are due primarily to the complete removal of EE2, which contributes most to the EEQ values.

### 3.2. Concentration of pharmaceuticals in STW effluent

It has been widely reported that the removal of pharmaceuticals during conventional sewage treatment is incomplete, sometimes as low as close to zero [13,27,28]. Of the 11 pharmaceutical compounds analysed, only five (propranolol, mebeverine, carbamazepine, indomethacine and diclofenac) were detected in pre-GAC effluent samples, and only three (propranolol, mebeverine, carbamazepine) were detected in post-GAC effluent samples. The concentrations of pharmaceuticals varied from 7.6 ng L<sup>-1</sup> for indomethacine, to 79.7 ng L<sup>-1</sup> carbamazepine, in pre-GAC effluents. In a study of three STWs in Ohio, USA, Spongberg and Witter [29] detected 34–111 ng L<sup>-1</sup> of carbamazepine in sewage effluents, which is comparable to the pre-GAC concentrations found in this study. In addition, the concentrations of carbamazepine in the effluent samples are significantly lower than those found elsewhere, with Kasprzyk-Hordern et al. [28] reporting concentrations up to 3117 ng L<sup>-1</sup> in the effluent of a STW in Cilfynydd, Wales and Zhou et al. [12] detecting 233–1061 ng L<sup>-1</sup> in the effluent of a STW in West Sussex, UK. For other pharmaceutical compounds, pre-GAC concentrations are broadly comparable to other studies, albeit at the lower-end of reported concentrations, such as 6–35 ng L<sup>-1</sup> for indomethacine [12,30].

The pharmaceutical concentrations were substantially reduced in post-GAC effluents, varying from <LOD for indomethacine and diclofenac to 47.6–58.4 ng L<sup>-1</sup> for carbamazepine. On average, the additional removal of pharmaceuticals by GAC was between 17% for propranolol to >98% for indomethacine (Fig. 3a). These reductions are broadly comparable to results derived from laboratory testing using activated carbon [16].

The concentrations of pharmaceuticals also varied diurnally, as shown during the 24-h sampling (Fig. 3b). Mebeverine varied from 33.39 to 41.5 ng L<sup>-1</sup> in pre-GAC effluents and 5.0–7.4 ng L<sup>-1</sup> in post-GAC effluents. The total concentrations of all measured pharmaceuticals did not vary as significantly as EDCs during either 24-h period, but similarly a peak of the total measured pharmaceutical compounds of 201.8 ng L<sup>-1</sup> at 22:00 in pre-GAC samples was observed, with even less variability in post-GAC effluents (RSD = 3.9%).

### 3.3. Concentrations of EDCs and pharmaceuticals in the receiving river waters

To assess the beneficial effect of GAC technology, the concentrations of EDC were determined in river water samples downstream

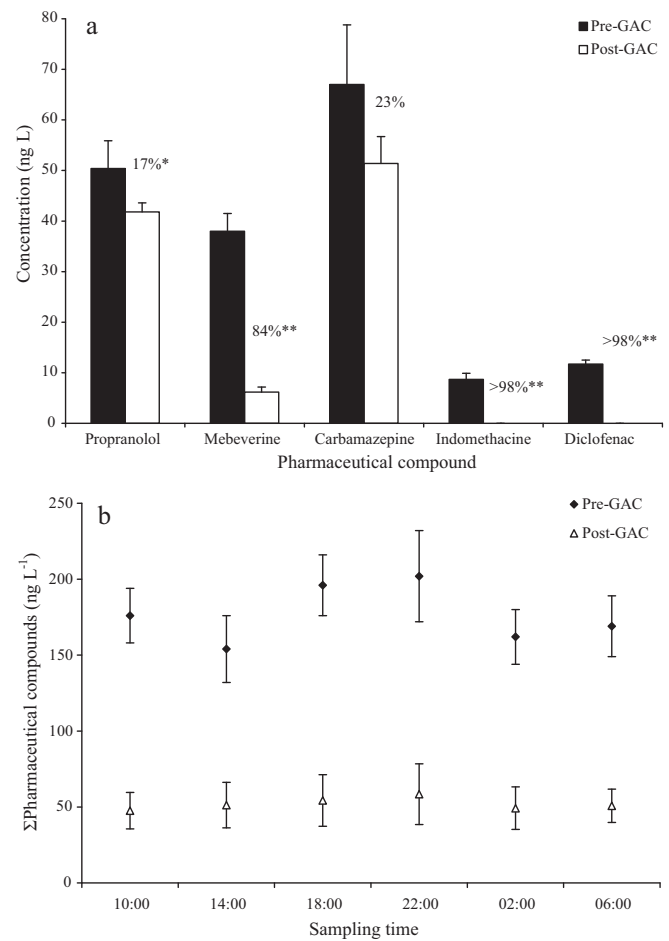


Fig. 3. (a) Comparison of the pre- and post-GAC effluent samples for: (a) mean concentrations of pharmaceutical compounds and (b) temporal variability of measured total pharmaceutical concentrations. Error bar = one standard deviation. Symbols \*\* and \* represent *P* values of <0.01 and <0.05, respectively.

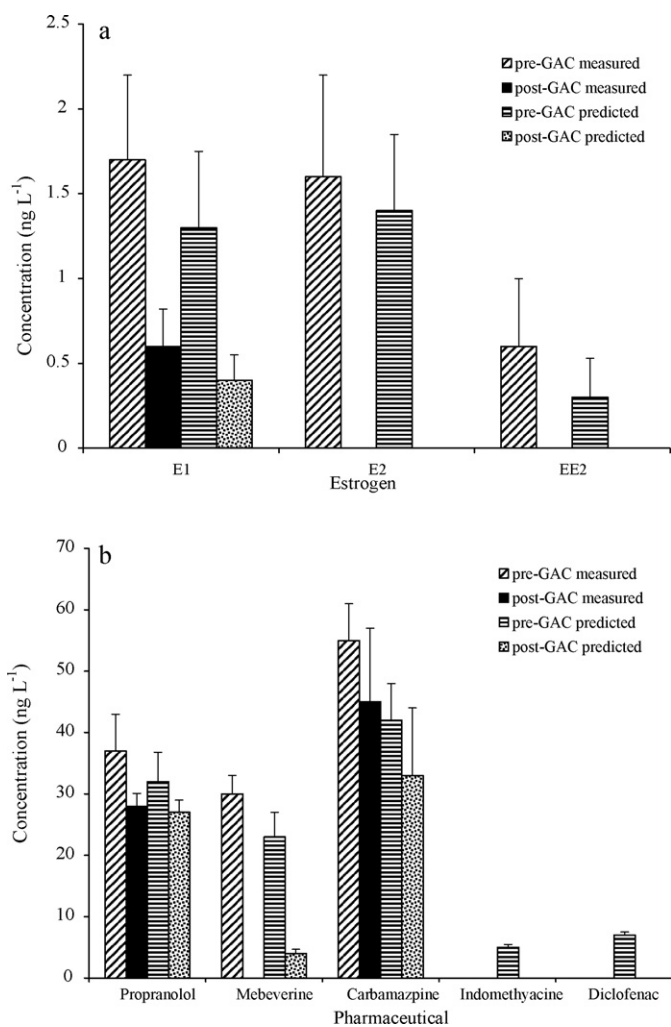
of the STW. Fig. 4a shows that, as expected, since sewage effluent was recognised as the predominant source of environmental estrogens in natural waters, the reduction in the measured concentrations of the steroidal estrogens observed in sewage effluent was reciprocated in the receiving river. A similar profile is shown in Fig. 4b for pharmaceuticals.

To evaluate the importance of STW as a point source of emerging contaminants in rivers, a simple dilution model, based on mass balance principles, was used to predict pollutant concentrations downstream of effluent discharge [12,31]:

$$C_{DW} = \frac{C_{UW} \times V_{UW} + C_{EF} \times V_{EF}}{V_{DW}} \quad (2)$$

where  $C_{EF}$ ,  $C_{UW}$ ,  $C_{DW}$  are the pollutant concentrations in the STW effluent, upstream and downstream.  $V_{EF}$ ,  $V_{UW}$  and  $V_{DW}$  represent the flow rates in the effluent, upstream and downstream.

Good agreement between measured and predicted concentrations was observed, particularly for the steroidal estrogens. For pharmaceuticals, the model prediction was excellent for propranolol, and still good for carbamazepine. Overall, however, the model tended to underestimate by between 5 and 28% for those compounds that were also detected by chemical measurement. On the other hand, the model predicted the presence of indomethacine and diclofenac at concentrations significantly above the method LOD in the receiving river water in pre-GAC samples, which differed from the observed non-detectable concentrations through measurement. The model however subsequently predicted these

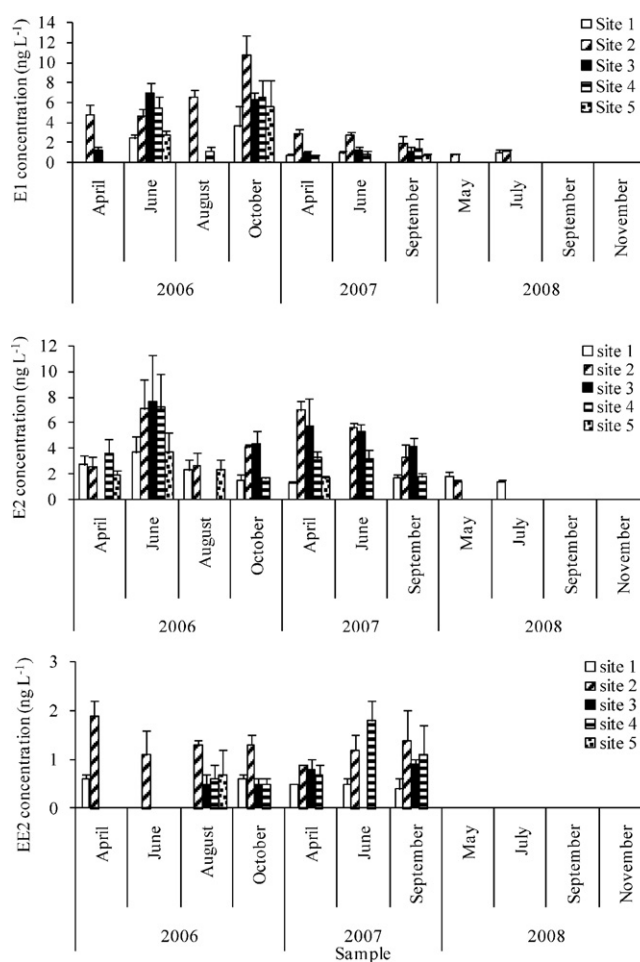


**Fig. 4.** Measured and predicted concentrations of: (a) steroidal estrogens and (b) pharmaceutical compounds 1.7-km downstream of the STW effluent, before and after GAC operation. Error bar = one standard deviation.

compounds would not be present in post-GAC samples, in agreement with the measured results. The model also predicted low concentrations (ng L<sup>-1</sup>) of mebeverine in the receiving river waters after GAC commission, which is an over-estimate in comparison to the measured results. Overall, the dilution model has provided a reasonable prediction of the measured EDC and pharmaceutical concentrations, demonstrating the importance of STW effluents as a point source of such compounds into the aquatic environment.

### 3.4. Temporal and spatial variation of EDC concentrations in the catchment waters

To fully appreciate the environmental occurrence and persistence of emerging contaminants in river water, as well as the added benefit of GAC installation, a systematic sampling and analysis of STW effluent and river water were undertaken. Results (Fig. 5) show the concentrations of E1, E2 and EE2 at four sites in the receiving river, including one upstream and three downstream sites, as well as at a control site over a three-year period. The results demonstrate a clear reduction in the average concentrations from 3.2 ng L<sup>-1</sup> (pre-GAC) to <0.6 ng L<sup>-1</sup> (post-GAC, 81% reduction) for E1, 3.8 ng L<sup>-1</sup> to <1.2 ng L<sup>-1</sup> (at least 68% reduction) for E2, and 0.8 to <0.4 ng L<sup>-1</sup> (at least 50% reduction) for EE2 downstream of the effluent, after the installation of the GAC plant. However, there appears to be a lag between the reduction in effluent concentrations and the appar-



**Fig. 5.** Concentrations of E1, E2 and EE2 across the catchment over the three year period. Site 1 = 3.5 km upstream, site 2 = 10 m downstream, site 3 = 1.7 km downstream, site 4 = 8.3 km downstream, site 5 = control site. Error bar = one standard deviation.

ent non-presence of E1 and E2 in the receiving river water, with a small amount of these compounds present in downstream samples some months after installation of the GAC. This is likely due to pre-existing amounts of these compounds from pre-GAC effluent taking some time to degrade. There appears to be no such lag for EE2, which was not detectable in any sample from the catchment after installation of the GAC.

## 4. Conclusions

A significant reduction in the concentrations of three key steroidal estrogens in sewage effluents, and subsequently in the receiving river waters, was observed because of the installation of GAC as a post-tertiary sewage treatment process. The impact of GAC in reducing the concentrations of pharmaceutical compounds in effluent samples was more variable; while some compounds were shown to be significantly removed, others were not, and removal appeared to vary between different classes of pharmaceuticals. Regular sampling in the river water downstream of effluent discharge also demonstrated a major reduction in the concentration of these compounds following the operation of the GAC plant. The importance of the STW as a key source of emerging contaminants in the river has been confirmed by both chemical analysis and by prediction from mathematical modelling. Further research is needed, however, as whether these reductions in contaminant concentrations are sufficient as to prevent endocrine disrupting effects in

aquatic organisms on the longer term, remains to be confirmed. Moreover, GAC-based removal technology will become less efficient over time for some classes of organic pollutants, including EDCs and pharmaceuticals, as adsorption sites become saturated. As of yet, the long-term efficacy of GAC for the removal of steroidal estrogens and pharmaceuticals is not fully understood, and existing analytical procedures are unable to detect and resolve concentrations of E2 or EE2 at concentrations likely to be present in post-GAC effluents. Analytical research should focus on further improving the sensitivity of analysis so that the behaviour of steroidal estrogens at these trace concentrations can be better understood. Cost implications (e.g. GAC) will also feature highly as a major driver in future investigations.

### Acknowledgements

This work was funded as part of the Endocrine Disruption in Catchments Programme (EDCAT), which is supported by the UK Department for Environment Food and Rural Affairs, and the Environment Agency of England and Wales (grant number CPEC-70).

### References

- [1] J.L. Oaks, M. Gilbert, M.Z. Virani, R.T. Watson, C.U. Meteyer, B.A. Ridesut, H.L. Shivaprasad, S. Ahmed, M.J.I. Chaudhry, M. Arshad, S. Mahmood, A. Ali, A.A. Khan, Diclofenac residues as the cause of vulture population decline in Pakistan, *Nature* 427 (2004) 630–633.
- [2] J.R. Lawrence, B. Zhu, G.D.W. Swerhone, J. Roy, L.I. Wassenaar, E. Topp, D.R. Korber, Comparative microscale analysis of the effects of triclosan and triclocarban on the structure and function of river biofilm communities, *Sci. Total Environ.* 407 (2009) 3307–3316.
- [3] V.L. Winder, Y. Sapozhnikova, P.L. Pennington, E.F. Wirth, Effects of fluoxetine exposure on serotonin-related activity in the Sheepshead Minnow (*Cyprinodon variegatus*) using LC/MS/MS detection and quantitation, *Comp. Biochem. Phys. (Part C)* 149 (2009) 559–565.
- [4] P. Burkhardt-Holm, Endocrine disruptors and water quality: a state-of-the-art review, *Water Res. Dev.* 26 (2010) 477–493.
- [5] C. Desbrow, E.J. Routledge, G. Brighty, J.P. Sumpter, M.J. Waldock, Identification of estrogenic chemicals in STW effluent. Chemical fractionation and in vitro biological screening, *Environ. Sci. Technol.* 32 (1998) 1549–1558.
- [6] K.V. Thomas, M. Hurst, P. Matthiessen, M.J. Waldock, Characterization of estrogenic compounds in water samples collected from United Kingdom estuaries, *Environ. Toxicol. Chem.* 20 (2001) 2165–2170.
- [7] J. Corcoran, M.J. Winter, C.R. Tyler, Pharmaceuticals in the aquatic environment: a critical review of the evidence for health effects in fish, *Crit. Rev. Toxicol.* 40 (2010) 287–304.
- [8] R.L. Gomes, M.D. Scrimshaw, J.N. Lester, Determination of endocrine disruptors in sewage treatment and receiving waters, *Trends Anal. Chem.* 22 (2003) 697–707.
- [9] A.C. Johnson, J.P. Sumpter, Removal of endocrine disrupting chemicals in activated sewage treatment works, *Environ. Sci. Technol.* 35 (2001) 4697–4703.
- [10] Z. Liu, Y. Kanjo, S. Mizutani, Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment – physical means, biodegradation, and chemical advanced oxidation: a review, *Sci. Total Environ.* 407 (2009) 731–748.
- [11] B. Kudlak, J. Namieśnik, Environmental fate of endocrine disrupting compounds—analytical problems and challenges, *Critic. Rev. Anal. Chem.* 38 (2008) 242–258.
- [12] J.L. Zhou, Z.L. Zhang, E. Banks, D. Grover, J.Q. Jiang, Pharmaceutical residues in wastewater treatment works effluents and their impact on receiving river water, *J. Hazard. Mater.* 166 (2009) 655–661.
- [13] D. Bendz, N.A. Paxeus, T.R. Ginn, F.J. Logec, Occurrence and fate of pharmaceutically active compounds in the environment, a case study: Hoje River in Sweden, *J. Hazard. Mater.* 122 (2005) 195–204.
- [14] A.S. Stasinakis, G. Gatidou, D. Mamais, N.S. Thomaidis, T.D. Lekkas, Occurrence and fate of endocrine disruptors in Greek sewage treatment plants, *Water Res.* 42 (2008) 1796–1804.
- [15] Y. Zhang, J.L. Zhou, Occurrence and removal of endocrine disrupting chemicals in wastewater, *Chemosphere* 73 (2008) 848–853.
- [16] S.A. Snyder, S. Adham, A.M. Redding, F.S. Cannon, J. DeCarolis, J. Oppenheimer, E.C. Wert, Y. Yoon, Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals, *Desalination* 202 (2007) 156–181.
- [17] M. Fuerhacker, A. Durauer, A. Jungbauer, Adsorption isotherms of 17 $\beta$ -estradiol on granular activated carbon (GAC), *Chemosphere* 44 (2001) 1573–1579.
- [18] Y. Zhang, J.L. Zhou, Removal of estrone and 17 $\beta$ -estradiol from water by adsorption, *Water Res.* 39 (2005) 3991–4003.
- [19] N. Nakada, T. Tanishima, H. Shinohara, K. Kiri, H. Takada, Pharmaceutical chemicals and endocrine disruptors in municipal wastewater in Tokyo and their removal during activated sludge treatment, *Water Res.* 40 (2006) 3297–3303.
- [20] A.C. Johnson, R.J. Williams, P. Simpson, R. Kanda, What difference might sewage treatment performance make to endocrine disruption in rivers? *Environ. Pollut.* 147 (2007) 194–202.
- [21] R. Liu, J.L. Zhou, A. Wilding, Simultaneous determination of endocrine disrupting phenolic compounds and steroids in water by solid phase extraction–gas chromatography–mass spectrometry, *J. Chromatogr. A* 1022 (2004) 179–189.
- [22] Z.L. Zhang, A. Hibberd, J.L. Zhou, Optimisation of derivatisation for the analysis of estrogenic compounds in water by solid-phase extraction–gas chromatography–mass spectrometry, *Anal. Chim. Acta* 577 (2006) 52–61.
- [23] Z.L. Zhang, J.L. Zhou, Simultaneous determination of various pharmaceutical compounds in water by solid-phase extraction–liquid chromatography–tandem mass spectrometry, *J. Chromatogr. A* 1154 (2007) 205–213.
- [24] A. Hibberd, K. Maskaoui, Z. Zhang, J.L. Zhou, An improved method for the simultaneous analysis of phenolic and steroidal estrogens in water and sediment, *Talanta* 77 (2009) 1315–1321.
- [25] D.P. Grover, Z.L. Zhang, J.W. Readman, J.L. Zhou, A comparison of three analytical techniques for the measurement of steroidal estrogens in environmental water samples, *Talanta* 78 (2009) 1204–1210.
- [26] R.J. Williams, V.D.J. Keller, A.C. Johnson, A.R. Young, M.G.R. Holmes, C. Wells, M. Gross-Sorokin, R. Benstead, A National risk assessment for intersex in fish arising from steroid estrogens, *Environ. Toxicol. Chem.* 28 (2009) 220–230.
- [27] T.A. Ternes, Occurrence of drugs in German sewage treatment plants and rivers, *Water Res.* 32 (1998) 3245–3260.
- [28] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, Multi-residue methods for the analysis of pharmaceuticals, personal care products and illicit drugs in surface water and wastewater by solid-phase extraction and ultra performance liquid chromatography–electrospray tandem mass spectrometry, *Anal. Bioanal. Chem.* 391 (2008) 1293–1308.
- [29] A.L. Spongberg, J.D. Witter, Pharmaceutical compounds in the wastewater process stream in Northwest Ohio, *Sci. Total Environ.* 397 (2008) 148–157.
- [30] Z.L. Zhang, A. Hibberd, J.L. Zhou, Analysis of emerging contaminants in sewage effluent and river water: comparison between spot and passive sampling, *Anal. Chim. Acta* 607 (2008) 37–44.
- [31] T. Heberer, Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, *Toxicol. Lett.* 131 (2002) 5–17.