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Natural Variations in Flow Are Critical in Determining Concentrations of Point Source Contaminants in Rivers: An Estrogen Example

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Daily steroid estrogen concentrations as 17β-estradiol equivalents (E2 equiv.) were modeled from 1992 to 2008 for single locations on the well populated Thames and Soar rivers in England. The historic daily mean flow values which were the basis of this exercise came from a selected gauging site on each river. The natural variation in flow from winter to summer typically produced a 20- to 30-fold difference in predicted estrogen concentration over the course of a year. Based on all the predicted values from minimum to maximum over the 1992 to 2008 period there was a 98-fold difference in estrogen concentrations on the basis of flow alone for the Thames (0.1−12.7 ng/L E2 equiv.) and 67-fold for the Soar (0.2−13.3 ng/L E2 equiv.). This compares to a predicted 0.5-fold difference that could arise from differences in sewage treatment and 0.1-fold difference due to differences in in-stream biodegradation. The seasonal variation in flow generated a repeating "roller coaster" in predicted estrogen concentrations. Regularly measured phosphate data for the river Avon over the period 1993 to 1996, where point sources also dominate, was compared against flow and predicted estrogen concentrations. The pattern of predicted estrogen and measured total phosphate concentration were very closely related. This dramatic variation in contaminant concentration over the year due to flow poses questions over what we mean by environmental relevance and the representation of the real environment in aquatic ecotoxicity tests.

Introduction

Until the mid 1990s the aquatic ecotoxicity and risk assessment of organic contaminants focused on persistent chemicals from industry and highly soluble pesticides which had a transient diffuse source. The phenomenon of endocrine disruption in fish and the identification of natural and xenobiotic endocrine disrupting chemicals in sewage effluent caused a dramatic change in emphasis (*1*). While there had always been an awareness of pollution incidents related to specific point sources, the endocrine disrupting chemicals revealed that sewage effluents could serve as perpetual point sources for hazardous chemicals throughout developed countries (*2*−*4*). Scientists working in the aquatic environment have now observed the same phenomenon with pharmaceuticals and personal care products (PPCPs) (*5*−*7*). Unfortunately, measuring such chemicals at concentrations in the low to sub ng/L range is both extremely expensive and challenging and can be considered something of a scientific "bottleneck" (*8*). This drawback helped stimulate developments of geographic information system (GIS) water quality models to assess the likely extent of exposure across catchments, regions and nations (*9*−*13*). These models demonstrated that where you looked would have a very important bearing on the outcome.

This study attempts to address a further potential complication which could have an important bearing on the effects of point source chemicals on wildlife and how we study them; the potential effect of the natural variation in river flow. This issue has been suggested as a major confounding factor in discrepancies between between modeled and measured point source chemical values in a catchment (*14*). Of particular interest is the diluting effect both within a year and between years. The significance of this question is highlighted by the phrase "environmentally relevant concentration". When an aquatic ecotoxicologist seeks to demonstrate the significance of their studies on the toxic effects of a chemical they are discussed in terms of their proximity to an environmentally relevant concentration (*15*−*19*). The environmentally relevant concentration referred to may well be a single "snapshot" high measurement taken from a river. This could indeed be an environmental concentration, but how relevant is it? More importantly, just what range and pattern of exposure do aquatic organisms actually face over the course of a year? Previous studies with limited repeat sampling of point source contaminants such as natural and xenobiotic estrogens have noted big concentration changes related to dilution (*20, 21*). But three or four samples from the same location over the course of a year still do not provide a complete picture of the likely pattern and range of concentrations possible. In this study historic flow data was combined with an assumed constant input of estrogens from the known human population to reconstruct exposures to local fish over a 16 year period for two river locations. The objectives of this study were (1) examine the varying percentage of treated sewage effluent content of two populous rivers in England(UK); (2) assess through prediction, the impact of changing flow patterns on likely estrogen concentrations, as an example point source chemical, over the period 1992 to 2008 in these rivers; (3) use existing, regularly measured, phosphate data from a third river to corroborate the impact of dilution on concentration of a largely point source chemical.

Materials and Methods

Predicting Effluent and Estrogen Content for the River Thames and Soar over a 16 Year Period. Methods to predict the discharge of steroid estrogens estrone (E1), 17β-estradiol (E2), and 17α-ethinyloestradiol (EE2) from the human population via sewage treatment plants (STPs) to receiving waters have already been developed (*22*) and tested successfully against real data (*20, 23*−*25*). The STPs upstream of any river gauging point, and more importantly, their associated human population served, is already known for any point in England and Wales (*11*). Thus, it is possible to calculate probable combined estrogen concentrations as E2 equivalents (E2 equiv) far into the past using recorded flow and human population data.

For this exercise, two UK rivers were selected, the Thames at Reading, about 30 km west of London, and the Soar downstream of the city of Leicester (Figure 1). Both of these locations are in regions with relatively high population density

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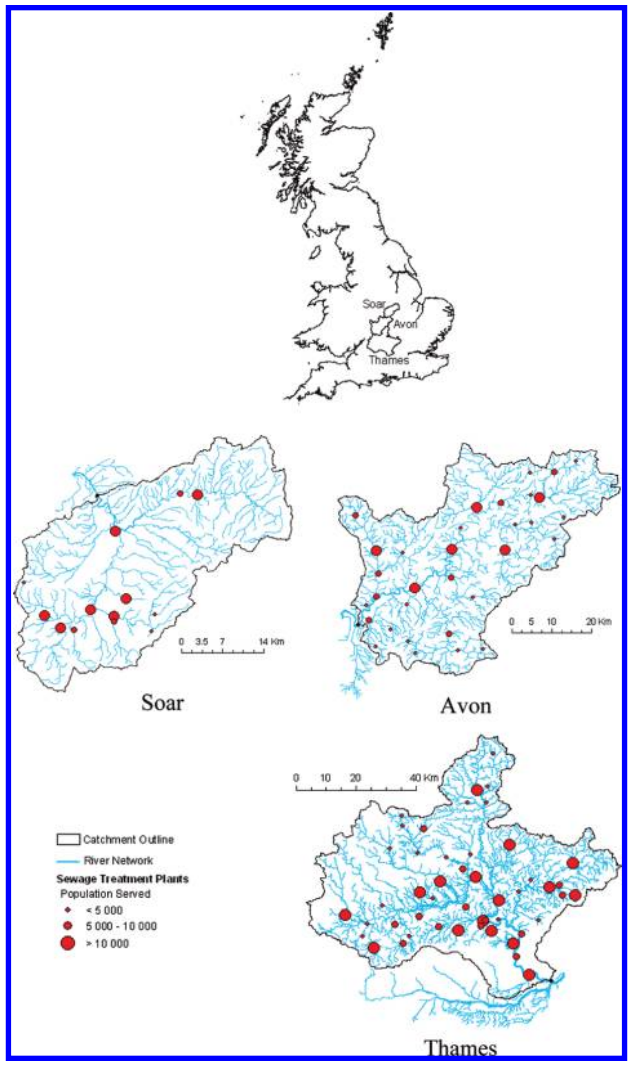

FIGURE 1. Maps of the catchments showing the boundaries, river network and location and size of STPs.

together with modest dilution and are where fish in the rivers are considered to be at risk of endocrine disruption (*11*). In other words, these river locations are where chemical, or wildlife monitoring might justifiably be carried out on point source contaminants of concern (Table 1).

For this exercise the following information was compiled to make the predictions: (1) The mean daily flow from January 1992 to December 2008; (2) The upstream human population; (3) An assumed constant per capita estrogen excretion (*22*) and final discharge which assumed all sewage treatment was by activated sludge treatment (*11*); (4) The daily estrogen concentration calculated by dividing the upstream estrogen loading by the daily mean flow values.

In this study the potential upstream contribution of agriculture to the estrogen loading was not considered. While potentially large, depending on the form of animal husbandry involved, the soil has been shown to be a very efficient remover of estrogens (*26*). It should be noted that the predicted estrogen concentrations provided here do not allow for in-stream sorption to sediments, or biodegradation (likely to cause an overestimation). Largely due to advection, even compounds with reasonably high K_d coefficients only lose a few percent to sediment sorption over tens of kilometers (*27*). Biodegradation appears to be the most important of the dissipation processes (*28*), but it needs a fairly long river to make a big impact on concentration (*27*) and here the rivers evaluated have main stems of only 30−100 km. This exercise does not differentiate the potentially under-performing biological (trickling) filters (*29*) within the catchment (likely to cause an under-estimation) from the activated sludge plants. It is also acknowledged that because dilution is the only factor determining concentration here, the effect of combined sewer overflows (CSOs) were not considered. Depending on location, intensity of rainfall events, and stormwater holding capacity these CSOs may play an important role in pushing contaminants out into the aquatic environment, particularly in hard rock catchments with steep elevations (*30*−*32*). Unfortunately, these data are not readily available in the UK and would be complicated to assess, since depending on the day/location some STPs in a catchment may experience a CSO, whereas others may not (*33*). Thus, to summarize, the assumptions used in this exercise were (1) That the only source of estrogens were the human population; (2) That the size of the human population was constant over the 16 year period; (3) That the per capita consumption/excretion of estrogens was constant over the 16 year period; (4) That the sewage treatment performance was constant over the 16 year period; (4) CSOs were not accounted for; (5) In-stream sorption and biodegradation of estrogens was not included.

Reviewing the Interaction of Phosphate As a Point Source Contaminant with Flow for the River Avon over a Four Year Period. As a means of corroborating the effects of fluctuations in river flow on the concentration of a (largely) point source chemical, some data on phosphate from a previous study on the River Avon was re-examined. The Avon has many similarities with the Soar and Thames catchments in terms of location (Figure 1), population density, rainfall and flow (Table 1). In contrast to organic microcontaminants such as estrogens, phosphate is relatively cheap and straightforward to measure. Fortnightly water samples were collected from the River Avon at Evesham over a period of 3 years from 1994 to 1996 (prior to phosphate stripping) and measured for total phosphate (Figure 1) as described by Bowes et al., 2005 (*34*). These data were then compared with the gauged flow on the same day (*34*).

Results and Discussion

Comparison of General Flow Characteristics between the Rivers and Their Populations. The rainfall and flow (runoff) is broadly proportional to the catchment area for the three rivers considered (Table 1). However, as a proportion, the Soar catchment is the most urbanised with a population

TABLE 1. General Flow Characteristics and Population of the Studied Rivers

river	gauging sta.	grid ref.	area (km2)	mean ann. rain. (mm)	upstream pop.	upstream urban area (%)	predicted upstream E2 equiv load/d (g)	mean flow (m3/s)	dilution per capita (m3/d/ca)[a]	Q50 (m3/s)	Q95 (m3/s)	Q10 (m3/s)
Thames	Reading 39130	SU718741	4634	693	991,811	3	3.46	37.5	3.3	22.8	5	97.4
Soar	Pillings Lock 28093	SK565182	1108	666	620,725	8	2.17	9.6	1.3	5.5	2.5	21.5
Avon	Evesham 54002	SP040438	2210	668	767,324	5	2.68	15.5	1.7	8.5	2.8	34.9

[a] Based on mean flow, these flow records and statistics are for the period from 1936 for the Avon, 1986 for the Soar and 1992 for the Thames gauging site until 2005.

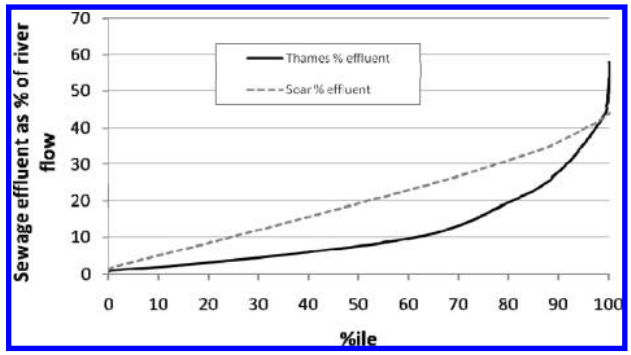

FIGURE 2. Treated sewage effluent as a percent of flow over 1992−2008 period for the River Thames at Reading and River Soar at Pillings Lock from mean daily flows.

density of 560/km^2 compared to 347/km^2 in the Avon and 214/km^2 in the Thames upstream of the chosen gauging points. Thus, the available daily dilution per capita in the River Soar which is around one-third of that available in the Thames, and about one-half of that in the Avon (Table 1). The difference between the Q95 low flow value (value exceeded 95% of the time) and Q10 high flow value (value only exceeded 10% of the time) was 19.5 for the Thames and only 12.5 for the Avon and 8.6 for the Soar indicating the Thames has a more variable flow regime (Table 1).

On the basis of the upstream human population and its per capita discharge it is possible to predict the proportion of treated effluent within the natural flow. The wide variation in this component can be seen in Figure 2 where at the 50th percentile mark the values for the River Thames at Reading comprises less than 10% sewage effluent in its total flow. While at the 80th percentile mark it rises to 20% effluent (1 in 5 dilution) with the 95th percentile point rising steeply to 35% effluent (less than 1 in 3 dilution).

Compared to the situation on the Thames, there is less dilution of sewage effluent available on the River Soar, at the 50%ile point the river would contain 20% effluent (1 in 5 dilution) with a linear rise to 40% effluent (2 in 5 dilution) at the 90th percentile mark (Figure 2). Therefore, the available dilution of sewage effluent would be routinely less than 1 in 10 in the River Soar and could be expected to be only 1 in 5, or 1 in 3, for large periods of time (Figure 2). It should be recalled that first tier risk assessment models typically used in chemical or pharmaceutical product registration such as EUSES (*35*) use a river water dilution factor of 1 in 10. For rivers in the UK, such as the Thames and Soar, this would underestimate risk and so could not be considered precautionary.

Predicted Estrogen Concentrations for the Rivers Thames and Soar Between 1993 and 2008. The predicted estrogen concentrations for the River Thames show a pronounced cyclical pattern (Figure 3). This variation corresponds with the seasonal cycle for flow to which the estrogen concentration is inversely related. The lowest predicted estrogen concentrations are observed typically in January at times of greatest flow and the highest in mid to late summer. Thus, based on these predictions it would appear that for half the months of the year the estrogen concentration will be below that which might be considered

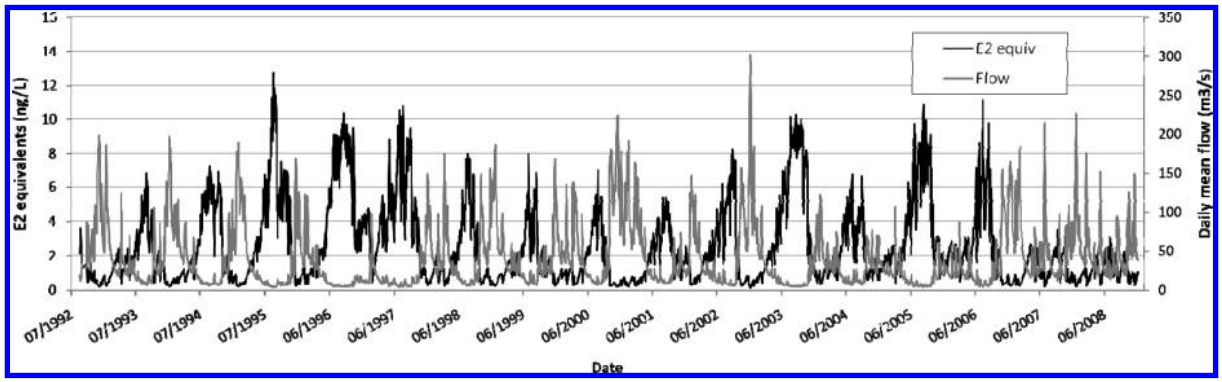

FIGURE 3. Predicted E2 equivalents for the River Thames at Reading for every day over the period 1992 to the end of 2008. Observed mean daily flows over the period are shown for comparison.

TABLE 2. Predicted Highest and Lowest E2 Equivalent Concentrations (ng/L) Based on Daily Mean Flow Measurements for the River Thames at Reading and River Soar at Pillings Lock

year	Thames highest E2 equiv	Thames lowest E2 equiv	difference (fold)	Soar highest E2 equiv	Soar lowest E2 equiv	difference (fold)
1992	3.62	0.21	17	12.64	0.37	34
1993	6.83	0.22	31	10.71	0.27	40
1994	7.27	0.21	35	8.90	0.34	26
1995	12.75	0.21	61	10.45	0.29	36
1996	10.32	0.33	31	12.77	0.68	19
1997	10.82	0.42	26	13.35	0.62	21
1998	7.94	0.27	29	9.87	0.20	49
1999	7.97	0.22	36	10.23	0.28	36
2000	7.03	0.18	39	10.33	0.24	43
2001	5.34	0.21	25	8.77	0.29	30
2002	7.92	0.22	36	10.66	0.28	38
2003	10.24	0.13	79	11.88	0.39	30
2004	6.76	0.33	20	9.97	0.40	25
2005	10.84	0.38	28	11.64	0.70	17
2006	11.14	0.26	43	9.69	0.46	21
2007	3.47	0.19	18	8.40	0.31	27
2008	3.02	0.18	17	11.08	0.30	37
overall	**12.75**	**0.13**	**98**	**13.35**	**0.20**	**67**

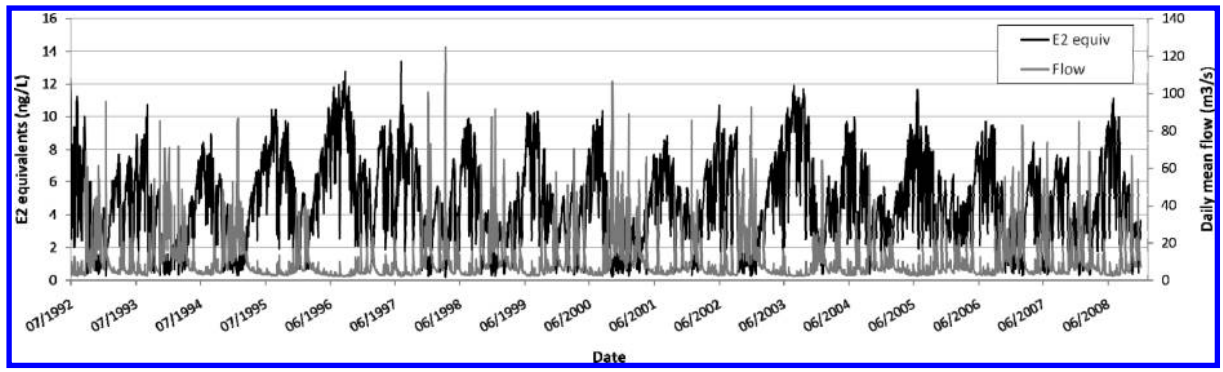

FIGURE 4. Predicted E2 equivalents for the River Soar at Pilling's Lock for every day over the period 1992 to end of 2008. Observed mean daily flows over the period are shown for comparison.

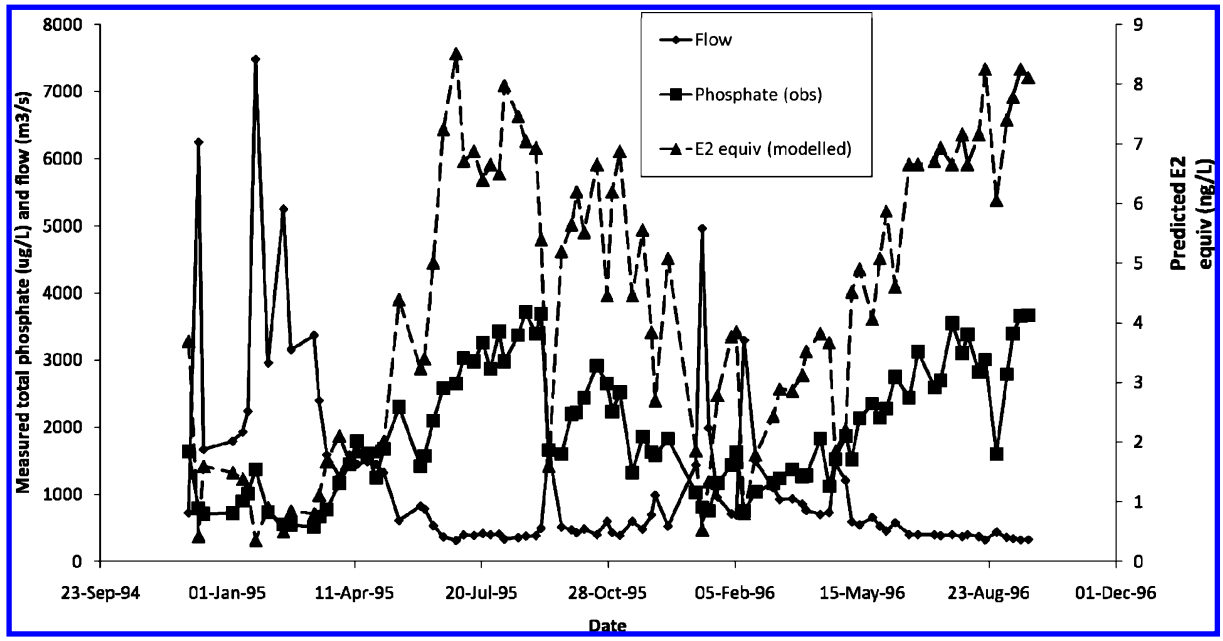

FIGURE 5. Measured flow, total phosphorus and modeled E2 equivalents for the River Avon at Evesham over the period of September 1994 to December 1996.

to have an effect (1 ng/L E2 equiv. (*11*)). Conversely, during the summer months, estrogen levels would be expected to routinely climb above 4 ng/L E2 equiv for three or more months of the year. Apart from seasonal changes, there can also be large differences between years, for example in 1997 for three summer months predicted concentrations ranged from 3 to 11 ng/L E2 equiv., whereas in the same months in 2007 they ranged from only 0.2 to 2.5 ng/L.

The estrogen river water concentration would be expected to vary typically 20- to 30-fold over the course of the year in the River Thames at Reading with the lowest difference being 17-fold, and the largest 79-fold within one year (Table 2). Over the 16 year period of 1992−2008 the biggest difference was 98-fold, a difference of almost 2 orders of magnitude. So the choice of both the month, and the year, will have an enormous impact on the measured concentration and wildlife exposure.

While not as dramatically cyclical as the River Thames, on the River Soar typically half the year the predicted concentrations are found between 4 and 6 ng/L E2 equiv. (Figure 4). In most years the highest predicted estrogen levels in the River Soar exceeded those in the River Thames (Table 2), and these higher levels persisted for longer. This pattern is what might have been expected given the higher population density of the Soar catchment and consequent lower mean dilution capacity (Table 1).

Comparing the Measurement of Phosphate As a Point Source Contaminant with Predicted Estrogens and Flow for the River Avon over a Four Year Period. Although phosphorus is not the perfect conservative solute, before the coming of the urban wastewater directive in Europe it was discharged in very large quantities in sewage effluent, and at least in its free ion form, highly mobile. Phosphorus is also discharged into the catchment from the diffuse source of agriculture following rainfall runoff events, but in most of the populous UK catchments, sewage effluent is seen as the major source (*36*) and particularly so in the Avon (*37*). Therefore, regular phosphorus measurements can give us an impression at least of the impact of changing natural river flow on the concentration of a point source chemical (Figure 5). With these real measurements, a clear inverse relationship of concentration with flow can be seen just as predicted for estrogens from their sewage point source. The trend in predicted estrogen concentration mirrored the actual measurements of total phosphate over this period (Figure 5). However, it can be noted that as a point source contaminant, the peak phosphate concentrations (at low flow) were less with respect to the high flow periods than that predicted for the estrogens. As described previously, in this prediction exercise the estrogens are modeled as a conservative solute. This apparent damping effect is likely to be related to river bed sediments and near river water

storage and recharge acting as a store for phosphate during low flow events, a loss calculated to be between 50 and 70% in summer for the River Thames (*38*).

Existing data on phosphorus where point sources are very important, clearly demonstrate the large impact natural variations in flow has on in-stream concentrations. Previous GIS based hydrological models have illustrated where you stand beside the river, or which region you go to take your sample will have a very important influence on the concentration measured for a point source chemical (*9*−*11*). In these well populated rivers of the Thames and Soar we can see that dilution of sewage effluent is routinely less than 10-fold. These rivers with their modest dilution capacity are by no means atypical of central and southern England (*11*). This assessment demonstrates that large differences in point source contaminant concentrations will occur at a single point in the river, in these cases potentially 30-fold, over the course of a year. Perhaps this should point us toward a greater use of passive samplers as being capable of integrating these signals as some have suggested (*25*)? Taking a single grab sample on one day in a dry summer, or a wet spring could be very misleading without reporting associated flow information.

It is worthwhile comparing this predicted 30-fold difference in the river water estrogen concentration due to flow with that which might be expected due to biodegradation. Using LF2000-WQX as set up by Williams et al 2009 (*11*) for the River Thames at Reading it was found that switching off biodegradation (half-lives of a few days for the natural estrogens) for the three steroid estrogens for this length of river would only change the concentration by a factor of 0.13. The performance of biological (trickling) filter treatment plants (BFPs) has been compared with high performance activated sludge plants (ASP) (*29*) and the difference in outcome formalized by in a catchment estrogen prediction model (*11*). Thus for the same input, the estradiol equivalent would be expected to be 21.4 ng/L for an ASP and 32.5 ng/L for a BFP, a 0.5-fold difference. Consequently the impact of river dilution would appear to be many times more important than that of either sewage treatment type, or in-stream biodegradation on influencing river estrogen concentrations, at least in a UK setting.

Not only the day, or month, but the year the sample is taken could also have a large influence on the result. For example, significant endocrine disruption effects might be expected in a fish in the Thames in 1997, but not in 2008 (Figure 3). What is clear is that aquatic wildlife in rivers with a sizable human population will face a "roller-coaster" exposure regime to point source chemicals such as estrogens and PPCPs. This cyclical trough and spike should give us pause for thought when the phrase "environmentally relevant" is used. Both the high summer peak concentration and the low winter concentration could be equally considered environmentally relevant. In the example of the Thames, this exposure regime might be considered as six months of high concentrations with a chemical followed by six months of depuration. Some thought has been given to the ecotoxicological impact of fluctuating exposure of estrogens and fish but so far to only a narrow concentration range and for a short duration (*39*). When considering the effects of point source chemicals on wildlife, not only is it necessary to grapple with mixtures of contaminants but also with dramatic fluctuations in their concentrations too!

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