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Elevated Risk from Estrogens in the Yodo River Basin (Japan) In Winter and Ozonation as a Management Option

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Abstract

A simple model was set up to predict estrogen concentrations and endocrine disruption risk for the Yodo River, Japan. This catchment spans the conurbations of Kyoto and Osaka and is the main source of drinking water for Osaka City, Japan. From the river survey data (5 separate occasions between 2005 and 2008), a maximum 32 g/day estrone (E1) load was observed in the most downstream site of the river. Predicted E1 concentrations were in reasonable agreement with the measurements taken at several points within the basin from a series of sampling campaigns. The predicted concentrations exceeded a net estradiol (E2) equivalent of 1 ng/L on only a few occasions, suggesting only limited endocrine disruption phenomena in fish along the Yodo River is likely. The model was then used to examine the impact on estrogen concentrations and endocrine disruption of a number of different scenarios. It was found that in-river biodegradation had little effect on predicted concentrations and the outcome of endocrine disruption along the catchment. However, reduced sewage treatment removal, as can be experienced in winter in Japan, led to levels of 3.1 ng/L E2 equivalents being possible. The reduced river flow in winter in Japan exacerbates the situation as it offers less dilution. It was found that the application of the ozonation process as a tertiary sewage treatment in winter could prevent this higher risk endocrine disruption situation.

Keywords

Natural Estrogens; Model; Yodo River; PEC; Risk Assessment; Estradiol Equivalents, Mass Load

1 INTRODUCTION

Given its high population density, and island status, there has been a persistent concern that Japanese river ecosystems will be highly exposed to micropollutants such as estrogens. Part of this concern derives from the extent and impact of endocrine disruption in England (UK) which is also a densely populated island[1,2]. However, the population distribution and rainfall pattern of Japan is different from the UK, so that for many rivers the risk is believed to be low[3]. Nevertheless, there are some catchments in Japan such as the Tone and Yodo Rivers which have dense human populations along their length which may represent high exposure areas[3].

Estrogens which pass through the sewage treatment plants (STPs) are believed to play a major role in endocrine disruption in the aquatic wildlife[4,1,5]. One of the major natural estrogens discharged into the surface water is estrone (E1)[6,7] and this is a particularly important component of the overall estrogenic potency of Japanese effluent in the virtual absence of synthetic estrogens[8]. Thus, it is considered that E1 and E2 remain as important contributors to endocrine disruption in fish including the intersex condition[4,9]. Hence, to assess risk of endocrine disruption in Japanese rivers E1 would be the most important chemical to focus on along with E2.

Because of the importance of natural estrogens in determining the estrogenic potency of STPs effluent, there have been a number of attempts to predict the concentration in the aquatic environment[10,1,11]. Previous studies have indicated dilution and biodegradation as being the most dominant processes[10,3,12,13]. Thus, from identifying and quantifying the sewage inputs, degradation rate in the river and collecting river flow information, it should be possible to predict concentrations of a natural estrogen or chemical contaminant throughout a catchment. Modelling contaminants in a real catchment and comparing the predictions to observations allows us to check whether our understanding of the chemical, its source, and behavior is correct. The performance of differing sewage tertiary treatments such as ozonation and activated charcoal in reducing endocrine disruption in fish gives grounds for encouragement[14]. But the application of such costly technologies would need to be applied with care and perhaps measurement and modeling can both guide when and where such interventions might produce the greatest benefits.

In this study we will evaluate the mass balance of E1 in the River catchment, develop a model for the river to help assess the current risk of endocrine disruption. In addition we will evaluate the impact of reduced in river biodegradation, or sewage treatment on river concentrations. Finally, we will model the impact of applying ozonation (as a tertiary treatment) in the catchment's STPs to reduce the estrogen risk in the river.

2 MATERIALS AND METHODS

2.1 Study Area

The Yodo River flows southwest crossing across the Kyoto City and Osaka City, two major cities of central Japan, before joining the Osaka Bay (Figure 1). The Yodo River has a catchment area of 8240 Km^2 and it is one of the largest rivers in Japan. The Yodo River catchment consists of three major tributaries, which are the Uji, Katsura and Kizu Rivers. The significance of Hirakata Bridge is that it is close to a major water abstraction point for Osaka and is located only 19 km from the first to several STPs in the catchment (7 to 18 h of water travel time). The distance of the sampling point at Hirakata Bridge is 22, 23 and 12 km downstream from the Uji River/Ingen Bridge, Katsura River/Katsura Bridge and from the Kizu River/Miyuki Bridge, respectively.

(Insert Figure 1)

2.2 Calculating estrogenic potency and loads in the Yodo catchment

Estrogenic potency for a mixture of natural and synthetic estrogens in terms of estradiol equivalents (E2 equiv) were calculated at each point in the Yodo River basin. Based on the approach used in Japan and the UK, the theoretical combined estrogenic activity from the major steroid estrogens was assumed to be[15,2]:

$$\text{E2 equiv} = [\text{E2}] + [\text{ethinyl estradiol}] \times 10 + [\text{E1}]/3 \qquad \text{Eq. 1}$$

Bracketed value shows the concentration of qualified estrogen in [ng/L]. Further, the load at each point was calculated by the following equation:

$$\text{Load} = \text{Estrogen concentration} \times \text{Flow} \qquad \text{Eq. 2}$$

The observed load [g/day] was calculated (for E1 and E2 equiv respectively) using the survey results as the concentrations and the flow rate of the day at each point (Eq. 2). The sewage effluent discharge rates of STPs at the day of the survey were obtained by submitting inquiries to the local government[16]. The flow rates of the rivers near by the sampling points were obtained from gauging stations carried out by Ministry of Land, Infrastructure, Transport and Tourism, Japan. In cases, where there were no gauging stations nearby, the flow rate measurement was performed by hand using a flow meter together with an estimation of the river cross section at that point.

2.3 Estrogen predictions in the Yodo catchment

To predict combined concentrations of E1 and E2 throughout the Yodo River basin, estrogen concentrations at STP outlets and discharge flow data were used as the starting points (7 STPs and 8 outlets). These data were obtained from the Yodo River survey[16] and used as the starting point of all the modeling estimations, in this study. The extent of dilution in the rivers was estimated by the river flow data with the 25th, 50th, 95th percentile flow at the Miyamae, Yodo and Hirakata Bridges (Table S1). The basic requirements of the model input are summarized in Table 1.

(Insert Table 1)

2.3.1 Selection of the rate constant for E1 in the river

There are several attenuation processes that could affect estrogens in the water column, but many studies have identified biodegradation as playing the principal role[17,13]. The approach taken here was to attribute observed changes to concentration not related to dilution, as being associated with biodegradation[13]. From the river survey data[16], 5 main downstream sampling points were selected to calculate the rate constant of estrogen degradation in each survey. The downstream points were, Miyamae Bridge, Tenzin Bridge, Yodo Bridge, Tango Bridge and Hirakata Bridge for Katsura River, Nishitakase River, Uji River, Yamashina River, and Yodo River, respectively (Figure 1). Loss in the rivers was considered by assuming a first order reaction. The first order rate reaction can be described as:

$$L_{Downstream} = L_1 \exp(-kt_1) + L_2 \exp(-kt_2) + ... + L_n \exp(-kt_n) \qquad \text{Eq. 3}$$

where $L_{Downstream}$ (µg/day) is the load at the downstream point, L_1 [µg/day] is the load at point 1. t [h] is the flow time and k [1/h] is the first order rate constant. The flow times (t) were derived from the relationship between the velocity and the distance (Table S2). The *k* values were calculated at 5 rivers in the basin: Uji, Yamashina, Katsura, Nishi Takase, and Yodo River. For the points where the concentrations were less than limits of detection (LODs) (not detected), LODs / 2 were applied.

E2 was not detected in the main river water and so an E2 decay rate could not be derived. Instead, for E2 decay a half-life of 1.2 d was used based on microcosm studies of English rivers[17]. In the case of the STP effluent loads, STP flow rate and E1 and E2 measurements were available. To introduce the influence of variations in river flow, which can be quite significant in Japan, predictions were made based on 25th, 50th and 95th percentiles using data from the gauged site (Table S1).

2.3.2 Removal efficiency of the contiguous STPs

The removal efficiencies for E1 and E2 were obtained from the surveys (composite sampling) conducted on 3 STPs located in Yodo River basin, where both influent and effluent samples were taken (Table 2).

(Insert Table 2)

For the remaining STPs (4 out of 7) effluent concentrations were obtained from the Yodo River survey[16] and then mean removal efficiencies were applied to estimate the estrogen concentrations in the influent. Influent concentrations were further applied for the estimation of effluent concentration in predicted scenarios (see section 2.4).

2.3.3 Calculations of river reach concentration

Based on input concentrations, dilution, flow time and degradation rate, the following equation[18] was used to estimate the predicted environmental concentration (PEC) at the three reference (Miyamae, Yodo and Hirakata Bridge) points.

$$C_{\mathrm{PEC}} = \frac{\sum (L_i e^{-k\tau_i})}{Q} \qquad \text{Eq. 4}$$

Where C_{PEC} =Predicted environmental concentration [ng/L], L_i= Mass loading from ith STP [ng/day], k = first order degradation rate constant [1/h], τ_i = flow time from the ith STP to the reference point [h], Q = flow rate [m^3/day].

2.4 Scenario selection for risk assessment and management scheme

To examine how environmental factors might affect the risk of endocrine disruption in the Yodo catchment and explore the impact of additional sewage tertiary treatment, a series of scenarios were set up. All the derived scenarios used 25th, 50th and 95th percentile flows to predict the environmental concentrations at downstream locations (reference points). The approach has been summarized in the Figure 2:

(Insert Figure 2)

- The first scenario represented the current conditions where the average estrogen decay constant was applied in the river. Concentrations were estimated at Miyamae Bridge (downstream of Katsura River), Yodo Bridge (downstream of Uji River) and Hirakata Bridge (downstream of Yodo River).
- The second scenario explored the impact of a decrease in sewage removal efficiency due to winter conditions. The decline in removal efficiency was obtained from[16], where a 3-fold increase in estrogen load during winter season was observed.

- In the third scenario, the average degradation (removal) rate during the transportation in the river was assumed to be zero; reflecting no estrogen degradation during transportation in the river.
- The forth scenario examined the potential impact of applying ozonation as a tertiary treatment in all STPs in the catchment. In this case, mean removal efficiencies of 89 and 97% were assumed for E1 and E2, respectively, in all STPs (Table 2).

3 RESULTS AND DISCUSSION

3.1 Estrogen load in the river basin scale

A high E1 discharged load was observed from STPs during the surveys performed on 5 separate occasions between 2005 and 2008 (Figure 3). This source would account for 90% of the E1 found in the Yodo River. It was found that the Nishitakase River had the highest levels of E1 load (Figure 3). The variation in additive mass load values from the STPs was also reflected in the further downstream sites of the river during each sampling campaign[16]. The maximum E1 load at the most downstream site (Hirakata Bridge) was observed in the Mar. 2005 (32 g/day), followed by the Dec. 2008 (17 g/day). E2 was detected at very few sampling points indicating E1 represents the greatest endocrine disruption threat in this catchment.

(Insert Figure 3)

The high E1 load in Mar. 2005 and Dec. 2008 in the river could be associated with the observed change in input load from STPs during the dry winter season[16]. This implies that the greatest E1 mass is transported into the Yodo River during the dry winter season.

3.2 E1 degradation in river water

The E1 degradation rate values had significant variation during the five sampling campaigns (Table 3). The average degradation rate was higher in Nishitakase River than that of other river tributaries. The Nishitakase River contains a very high proportion of effluent water from the adjacent STPs. Perhaps the differences in the degradation rate between the rivers were due to differences in the active microbial population composition in the different rivers[17]. Where an apparent 'negative rate' was observed (E1 apparently being formed in the river) this may be an artifact related to the limitations of grab sampling. Another possibility is that the effluent from unrestricted septic tanks may increase E1 concentrations in the tributaries. Similar trends were also observed in the same river catchment for some pharmaceuticals and personal care products (PPCPs)[19].

(Insert Table 3)

3.3 Reduction estimation and modeled E1 concentrations in Yodo River

As a first estimate, the concentrations loss (percent) was calculated during the five samplings campaigns. Given flow and transit time, 58 (±7.5), 98 (±0.9) and 97% (±0.5) E1 reduction would be expected up to Miyamae (Katsura River reach), Yodo (Uji River reach) and Hirakata Bridge (whole Yodo River catchment), respectively. This result implies that, except in the Katsura River, a significant dilution was available to account the input concentrations of E1 in the catchment and sub-catchment[16]. There was a good correlation (R^2=0.95) between the estimated concentration and the measured concentrations (n=12) at Miyamae Bridge, Yodo Bridge, and Hirakata Bridge (Figure 4). Thus, changes in river concentration could be accounted for by dilution and degradation alone. The predictions showed a slight tendency to underestimate the actual concentration.

This could be because the model used fixed 50%ile flow to estimate the concentrations and influence from the tributaries was not considered in the outcomes. However, the variation was within the acceptable level (<25% of normal) and could therefore provide more reliable results.

(Insert Figure 4)

3.4 Scenario based PECs in Yodo River basin

The low sewage removal scenario as might occur in winter (scenario 2) had a large impact on elevating estrogen concentrations and hence 'at risk' compared to current day (scenario 1) (Figure 5). The maximum concentration was estimated at 3.1 ng/L E2 equiv at Miyamae Bridge with 50th percentile flow, which is higher than the environmental risk level of concern of 1 ng/L E2 equiv[1,20]. Same time, the concentration was 0.8 ng/L E2 equiv at Hirakata with the same percentile flow. However, with 25th percentile low flow the PEC could exceed the 1 ng/L E2 equiv limit at Hirakata Bridge. When no river biodegradation was assumed (Scenario 3), the PEC with 50th percentile river flow changed little from the current condition. This phenomena reveals the density of STPs in the river basin and relatively short flow time available for biodegradation. Applying the ozonation tertiary treatment to all upstream STPs was predicted to more than halve the E1 concentrations compared to current conditions. The oxidation of organic micropollutants by ozonation tertiary treatment has been reported to be an efficient process to improve the removal efficiencies of the STPs[21–23]. Looking at these modelling results, and given the expense of ozonation one recommendation might be to use it only in winter when the biological performance of STPs as at its weakest, and dilution lowest.

(Insert Figure 5)

4 CONCLUSIONS

The agreement between the observed and predicted E1 in the Yodo River catchment shows that the load is dominated by municipal STPs. Thus, overall agriculture and septic tanks must play only a minor role. Relatively high E1 load in the downstream site of the Yodo River during the winter seasons suggests that consideration should be given to optimizing current sewage treatment to reduce the E1 discharge during this season. The simple model applied to a river basin was able to adequately predict E1 river concentrations. For the Yodo catchment the predicted and observed E1 and hence endocrine disruption potential are not overly alarming except in winter conditions. Although it is difficult to be certain, this is probably not the most dangerous biological window for the initiation of endocrine disruption. However, this exercise has demonstrated that a tertiary advanced oxidation process could be very helpful at reducing this winter scenario risk to acceptable levels.

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Figure Captions

Figure 1 Yodo River basin, Japan.

Figure 2 Different scenarios examined in PEC estimations.

Figure 3 Discharge Load of E1 in the Yodo River System during five sampling campaigns (From March 2005 to Dec. 2008) (All values are shown in g/day).

Figure 4 Comparison between the measured (dots) and estimated (lines) E1 concentrations obtained from the model at Miyamae, Yodo and Hirakata Bridge.

Figure 5 PEC of E1 and E2 equiv (in box) obtained from the model with 50th percentile flow (The error bars represent the 25th and 95th percentile PEC values).

Table 1 Summary of key inputs for the model

1	Estrogen removal	:Removal efficiency of the natural estrogens in the STPs and discharge load of the natural estrogens in the catchment
2	Degradation rate constant	:Degradation rate constants derived from actual field data
3	Yodo River flow data	:Mean flow, mean flow velocity, flow time to the reference points from the STPs within the catchment

Table 2 Estrogen removals (%) in surveyed STPs

Year	STP	E1 (ng/L)			E2 (ng/L)		
		Inf.	**Eff.**	**R.E. (%)**	**Inf.**	**Eff.**	**R.E. (%)**
2007	STP D	40.9	14.8	63.8	54.7	5.8	89.4
	STP B*	30.5	0.7	97.7	27.3	0.5	98.2
2008	STP D (1)	69.1	22.5	67.4	62.4	6.6	89.4
	STP B*	19.5	1.2	93.8	37.3	1.0	97.3
	STP C*	16.7	2.9	82.6	60.7	2.3	96.2
2009	STP D (1)	31.1	9.9	68.2	62.4	7.7	87.7
	STP B*	12.5	2.1	83.2	38.9	1.3	96.7
			Mean	79.5			93.5
			Mean*	89.2			97.1

Inf.= Influent

Eff.= Effluent

R.E.= Removal Efficiency

*STPs having Ozonation process as a tertiary treatment

Table 3 First order rate constants derived from Yodo River survey[16]

River	Survey	k(1/h) E1
Katsura	2005 Mar.	0.038
	2005 Nov.	0.031
	2006 Sep.	0.059
	2007 Nov.	0.273
	2008 Dec.	0.044
Nishitakase	2005 Mar.	NA
	2005 Nov.	0.121
	2006 Sep.	0.100
	2007 Nov.	0.349
	2008 Dec.	0.069
Uji	2005 Mar.	-0.041
	2005 Nov.	0.128
	2006 Sep.	-0.020
	2007 Nov.	-0.015
	2008 Dec.	-0.022
Yamashina	2005 Mar.	0.113
	2005 Nov.	0.295
	2006 Sep.	0.222
	2007 Nov.	-0.100
	2008 Dec.	-0.020
Yodo	2005 Mar.	0.006
	2005 Nov.	0.045
	2006 Sep.	-0.037
	2007 Nov.	-0.007
	2008 Dec.	0.042

k= First order rate constant

NA= Not Available

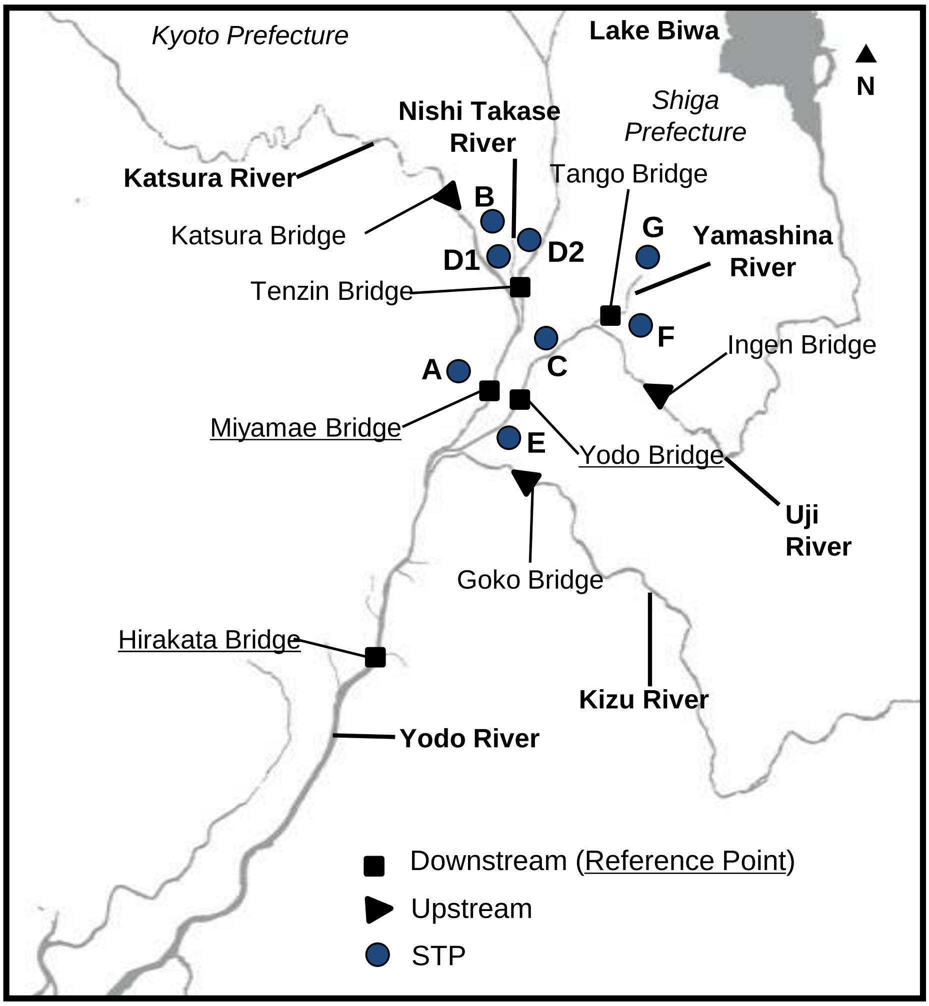


Figure 1 Yodo River basin, Japan.

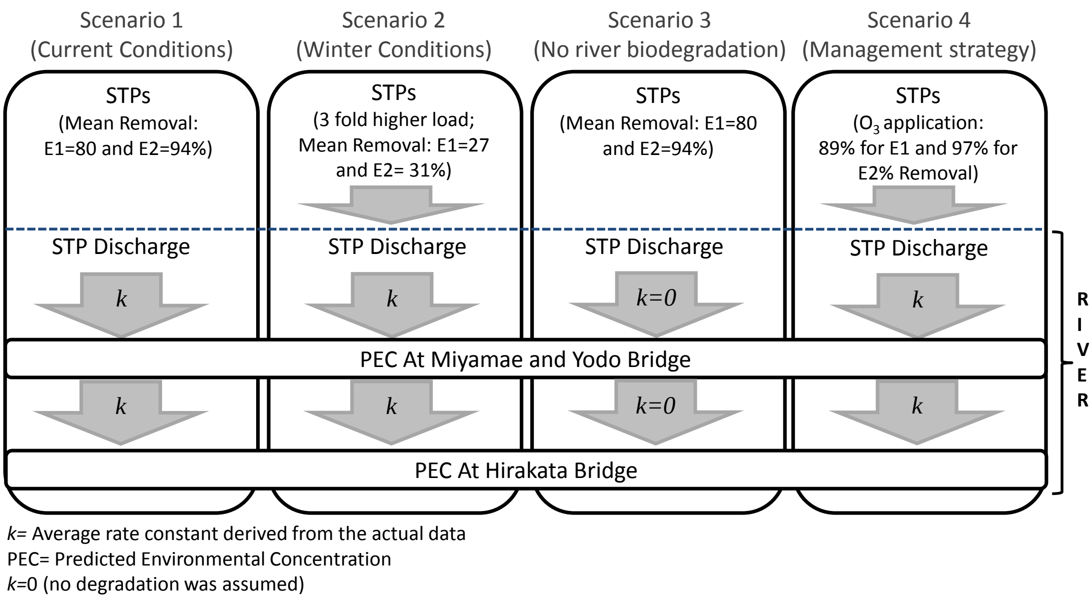
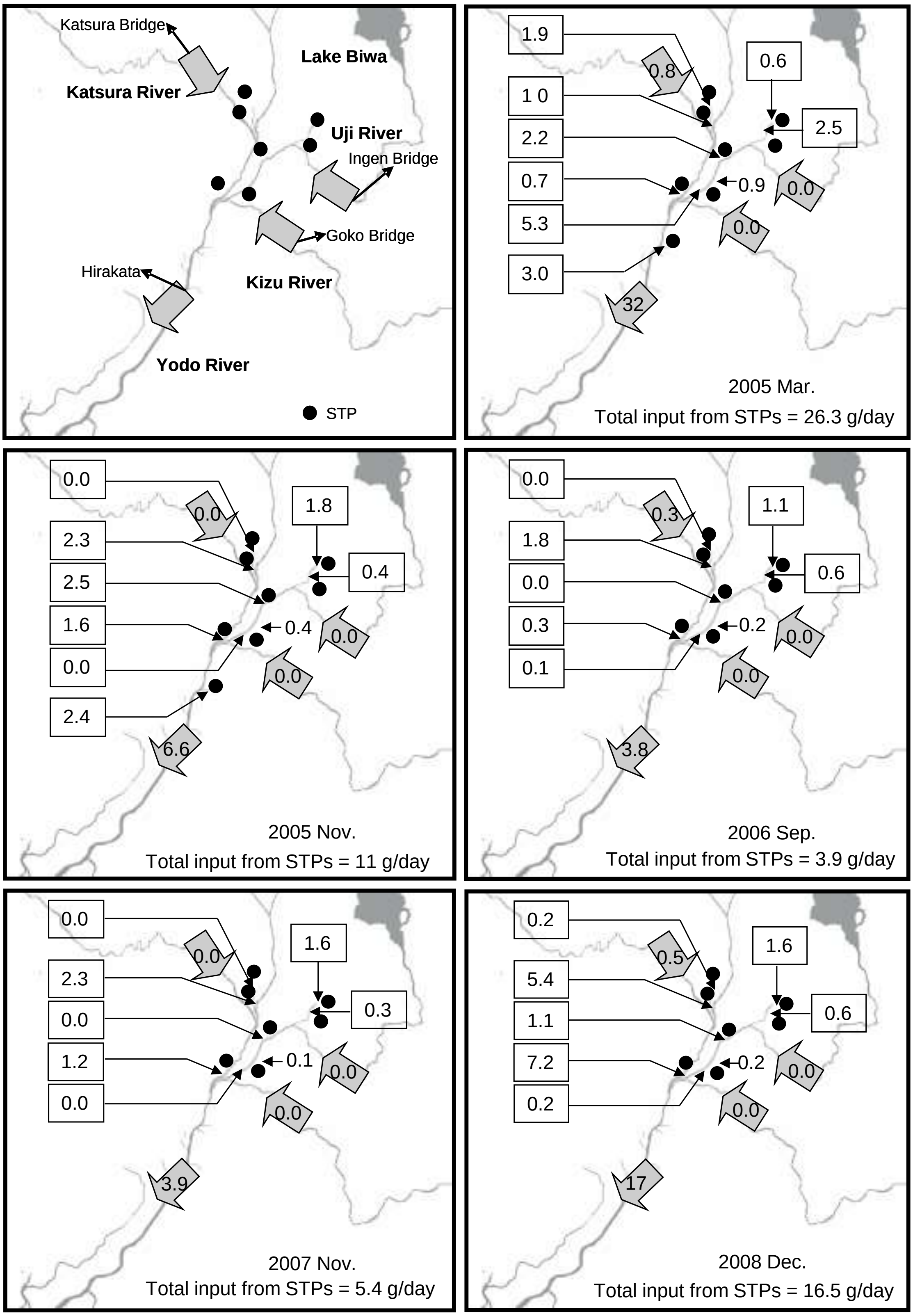
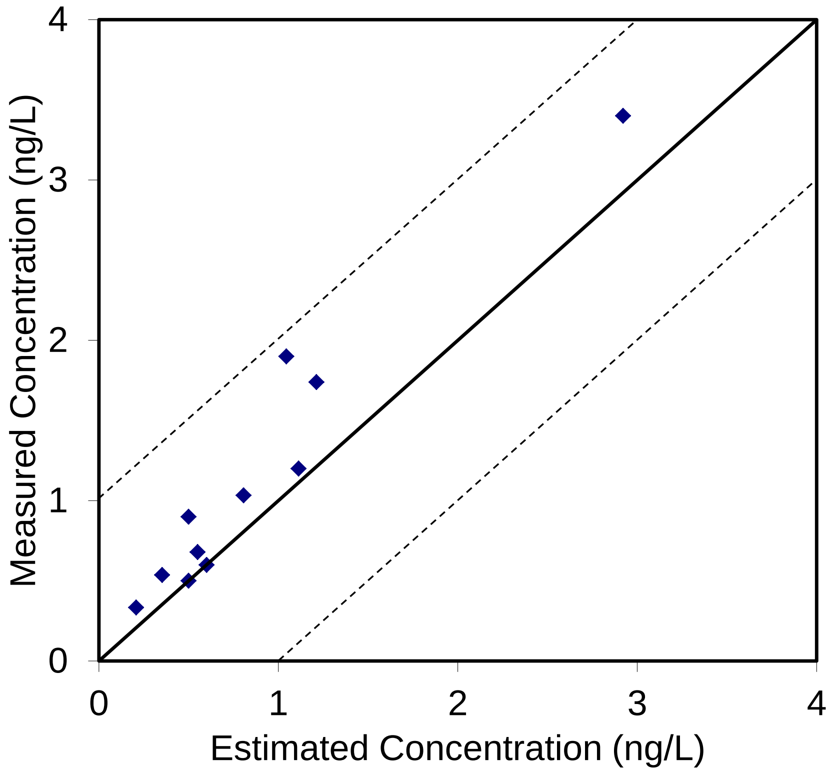


Figure 2 Different scenarios examined in PEC estimations.



Values inside the arrows: Load coming in and going out from the catchment
Values inside the boxes: Load observed in the STPs discharged water

Figure 3 Discharge Load of E1 in the Yodo River System during five sampling campaigns (From Mar. 2005 to Dec. 2008) (All values are shown in g/day).



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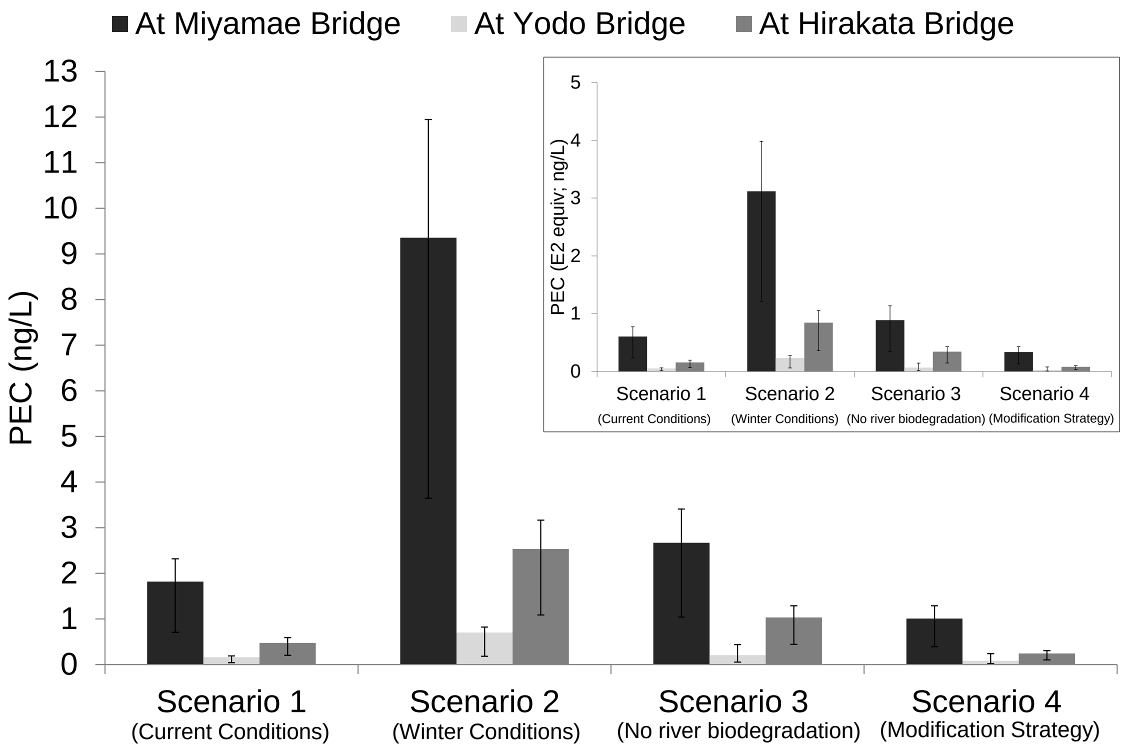

Figure 5 PEC of E1 and E2 equiv (in box) obtained from the model with 50th percentile flow (The error bars represent the 25th and 95th percentile PEC values).