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1 **Elevated Risk from Estrogens in the Yodo River Basin (Japan)**

2 **In Winter and Ozonation as a Management Option**

3

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17

18

Abstract

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

37

38

39

40 **Keywords**

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

43

44 **1 INTRODUCTION**

45 Given its high population density, and island status, there has been a persistent concern
46 that Japanese river ecosystems will be highly exposed to micropollutants such as
47 estrogens. Part of this concern derives from the extent and impact of endocrine disruption
48 in England (UK) which is also a densely populated island^{1,2}. However, the population
49 distribution and rainfall pattern of Japan is different from the UK, so that for many rivers
50 the risk is believed to be low³. Nevertheless, there are some catchments in Japan such as
51 the Tone and Yodo Rivers which have dense human populations along their length which
52 may represent high exposure areas³.

53

54 Estrogens which pass through the sewage treatment plants (STPs) are believed to play a
55 major role in endocrine disruption in the aquatic wildlife^{4,1,5}. One of the major natural
56 estrogens discharged into the surface water is estrone (E1)^{6,7} and this is a particularly
57 important component of the overall estrogenic potency of Japanese effluent in the virtual
58 absence of synthetic estrogens⁸. Thus, it is considered that E1 and E2 remain as important
59 contributors to endocrine disruption in fish including the intersex condition^{4,9}. Hence, to
60 assess risk of endocrine disruption in Japanese rivers E1 would be the most important
61 chemical to focus on along with E2.

62

63 Because of the importance of natural estrogens in determining the estrogenic potency of
64 STPs effluent, there have been a number of attempts to predict the concentration in the
65 aquatic environment^{10,1,11}. Previous studies have indicated dilution and biodegradation as
66 being the most dominant processes^{10,3,12,13}. Thus, from identifying and quantifying the
67 sewage inputs, degradation rate in the river and collecting river flow information, it
68 should be possible to predict concentrations of a natural estrogen or chemical contaminant

69 throughout a catchment. Modelling contaminants in a real catchment and comparing the
70 predictions to observations allows us to check whether our understanding of the chemical,
71 its source, and behavior is correct. The performance of differing sewage tertiary
72 treatments such as ozonation and activated charcoal in reducing endocrine disruption in
73 fish gives grounds for encouragement¹⁴. But the application of such costly technologies
74 would need to be applied with care and perhaps measurement and modeling can both
75 guide when and where such interventions might produce the greatest benefits.

76

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

82

83 **2 MATERIALS AND METHODS**

84 **2.1 Study Area**

85 The Yodo River flows southwest crossing across the Kyoto City and Osaka City, two
86 major cities of central Japan, before joining the Osaka Bay (Figure 1). The Yodo River
87 has a catchment area of 8240 Km² and it is one of the largest rivers in Japan. The Yodo
88 River catchment consists of three major tributaries, which are the Uji, Katsura and Kizu
89 Rivers. The significance of Hirakata Bridge is that it is close to a major water abstraction
90 point for Osaka and is located only 19 km from the first to several STPs in the catchment
91 (7 to 18 h of water travel time). The distance of the sampling point at Hirakata Bridge is
92 22, 23 and 12 km downstream from the Uji River/Ingen Bridge, Katsura River/Katsura
93 Bridge and from the Kizu River/Miyuki Bridge, respectively.

94

95

(Insert Figure 1)

96

97 **2.2 Calculating estrogenic potency and loads in the Yodo catchment**

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

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

102

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

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

105

106 The observed load [g/day] was calculated (for E1 and E2 equiv respectively) using the
107 survey results as the concentrations and the flow rate of the day at each point (Eq. 2). The
108 sewage effluent discharge rates of STPs at the day of the survey were obtained by
109 submitting inquiries to the local government¹⁶. The flow rates of the rivers near by the
110 sampling points were obtained from gauging stations carried out by Ministry of Land,
111 Infrastructure, Transport and Tourism, Japan. In cases, where there were no gauging
112 stations nearby, the flow rate measurement was performed by hand using a flow meter
113 together with an estimation of the river cross section at that point.

114

115 **2.3 Estrogen predictions in the Yodo catchment**

116 To predict combined concentrations of E1 and E2 throughout the Yodo River basin,
117 estrogen concentrations at STP outlets and discharge flow data were used as the starting
118 points (7 STPs and 8 outlets). These data were obtained from the Yodo River survey¹⁶
119 and used as the starting point of all the modeling estimations, in this study. The extent of
120 dilution in the rivers was estimated by the river flow data with the 25th, 50th, 95th
121 percentile flow at the Miyamae, Yodo and Hirakata Bridges (Table S1). The basic
122 requirements of the model input are summarized in Table 1.

123

124

(Insert Table 1)

125

126 *2.3.1 Selection of the rate constant for E1 in the river*

127 There are several attenuation processes that could affect estrogens in the water column,
128 but many studies have identified biodegradation as playing the principal role^{17,13}. The
129 approach taken here was to attribute observed changes to concentration not related to
130 dilution, as being associated with biodegradation¹³. From the river survey data¹⁶, 5 main
131 downstream sampling points were selected to calculate the rate constant of estrogen
132 degradation in each survey. The downstream points were, Miyamae Bridge, Tenzin
133 Bridge, Yodo Bridge, Tango Bridge and Hirakata Bridge for Katsura River, Nishitakase
134 River, Uji River, Yamashina River, and Yodo River, respectively (Figure 1). Loss in the
135 rivers was considered by assuming a first order reaction. The first order rate reaction can
136 be described as:

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

137 where $L_{Downstream}$ ($\mu\text{g}/\text{day}$) is the load at the downstream point, L_1 [$\mu\text{g}/\text{day}$] is the load at
138 point 1. t [h] is the flow time and k [1/h] is the first order rate constant. The flow times (t)
139 were derived from the relationship between the velocity and the distance (Table S2). The

140 *k* values were calculated at 5 rivers in the basin: Uji, Yamashina, Katsura, Nishi Takase,
141 and Yodo River. For the points where the concentrations were less than limits of
142 detection (LODs) (not detected), LODs / 2 were applied.

143

144 E2 was not detected in the main river water and so an E2 decay rate could not be derived.
145 Instead, for E2 decay a half-life of 1.2 d was used based on microcosm studies of English
146 rivers¹⁷. In the case of the STP effluent loads, STP flow rate and E1 and E2 measurements
147 were available. To introduce the influence of variations in river flow, which can be quite
148 significant in Japan, predictions were made based on 25th, 50th and 95th percentiles
149 using data from the gauged site (Table S1).

150

151 *2.3.2 Removal efficiency of the contiguous STPs*

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

155

156 **(Insert Table 2)**

157

158 For the remaining STPs (4 out of 7) effluent concentrations were obtained from the Yodo
159 River survey¹⁶ and then mean removal efficiencies were applied to estimate the estrogen
160 concentrations in the influent. Influent concentrations were further applied for the
161 estimation of effluent concentration in predicted scenarios (see section 2.4).

162

163 *2.3.3 Calculations of river reach concentration*

164 Based on input concentrations, dilution, flow time and degradation rate, the following
165 equation¹⁸ was used to estimate the predicted environmental concentration (PEC) at the
166 three reference (Miyamae, Yodo and Hirakata Bridge) points.

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

167 Where C_{PEC} = Predicted environmental concentration [ng/L], L_i = Mass loading from i th
168 STP [ng/day], k = first order degradation rate constant [1/h], τ_i = flow time from the i th
169 STP to the reference point [h], Q = flow rate [m³/day].

170

171 **2.4 Scenario selection for risk assessment and management scheme**

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

177

178

179

(Insert Figure 2)

180 • The first scenario represented the current conditions where the average estrogen decay
181 constant was applied in the river. Concentrations were estimated at Miyamae Bridge
182 (downstream of Katsura River), Yodo Bridge (downstream of Uji River) and Hirakata
183 Bridge (downstream of Yodo River).

184 • The second scenario explored the impact of a decrease in sewage removal efficiency
185 due to winter conditions. The decline in removal efficiency was obtained from¹⁶,
186 where a 3-fold increase in estrogen load during winter season was observed.

187 • In the third scenario, the average degradation (removal) rate during the transportation
188 in the river was assumed to be zero; reflecting no estrogen degradation during
189 transportation in the river.

190 • The fourth scenario examined the potential impact of applying ozonation as a tertiary
191 treatment in all STPs in the catchment. In this case, mean removal efficiencies of 89
192 and 97% were assumed for E1 and E2, respectively, in all STPs (Table 2).

193

194 **3 RESULTS AND DISCUSSION**

195 **3.1 Estrogen load in the river basin scale**

196 A high E1 discharged load was observed from STPs during the surveys performed on 5
197 separate occasions between 2005 and 2008 (Figure 3). This source would account for
198 90% of the E1 found in the Yodo River. It was found that the Nishitakase River had the
199 highest levels of E1 load (Figure 3). The variation in additive mass load values from the
200 STPs was also reflected in the further downstream sites of the river during each sampling
201 campaign¹⁶. The maximum E1 load at the most downstream site (Hirakata Bridge) was
202 observed in the Mar. 2005 (32 g/day), followed by the Dec. 2008 (17 g/day). E2 was
203 detected at very few sampling points indicating E1 represents the greatest endocrine
204 disruption threat in this catchment.

205

206 **(Insert Figure 3)**

207

208 The high E1 load in Mar. 2005 and Dec. 2008 in the river could be associated with the
209 observed change in input load from STPs during the dry winter season¹⁶. This implies that
210 the greatest E1 mass is transported into the Yodo River during the dry winter season.

211

212 **3.2 E1 degradation in river water**

213 The E1 degradation rate values had significant variation during the five sampling
214 campaigns (Table 3). The average degradation rate was higher in Nishitakase River than
215 that of other river tributaries. The Nishitakase River contains a very high proportion of
216 effluent water from the adjacent STPs. Perhaps the differences in the degradation rate
217 between the rivers were due to differences in the active microbial population composition
218 in the different rivers¹⁷. Where an apparent ‘negative rate’ was observed (E1 apparently
219 being formed in the river) this may be an artifact related to the limitations of grab
220 sampling. Another possibility is that the effluent from unrestricted septic tanks may
221 increase E1 concentrations in the tributaries. Similar trends were also observed in the
222 same river catchment for some pharmaceuticals and personal care products (PPCPs)¹⁹.

223

224 **(Insert Table 3)**

225

226 **3.3 Reduction estimation and modeled E1 concentrations in Yodo River**

227 As a first estimate, the concentrations loss (percent) was calculated during the five
228 samplings campaigns. Given flow and transit time, 58 (± 7.5), 98 (± 0.9) and 97% (± 0.5)
229 E1 reduction would be expected up to Miyamae (Katsura River reach), Yodo (Uji River
230 reach) and Hirakata Bridge (whole Yodo River catchment), respectively. This result
231 implies that, except in the Katsura River, a significant dilution was available to account
232 the input concentrations of E1 in the catchment and sub-catchment¹⁶. There was a good
233 correlation ($R^2=0.95$) between the estimated concentration and the measured
234 concentrations ($n=12$) at Miyamae Bridge, Yodo Bridge, and Hirakata Bridge (Figure 4).
235 Thus, changes in river concentration could be accounted for by dilution and degradation
236 alone. The predictions showed a slight tendency to underestimate the actual concentration.

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

241

242

(Insert Figure 4)

243

244 **3.4 Scenario based PECs in Yodo River basin**

245 The low sewage removal scenario as might occur in winter (scenario 2) had a large
246 impact on elevating estrogen concentrations and hence 'at risk' compared to current day
247 (scenario 1) (Figure 5). The maximum concentration was estimated at 3.1 ng/L E2 equiv
248 at Miyamae Bridge with 50th percentile flow, which is higher than the environmental risk
249 level of concern of 1 ng/L E2 equiv^{1,20}. Same time, the concentration was 0.8 ng/L E2
250 equiv at Hirakata with the same percentile flow. However, with 25th percentile low flow
251 the PEC could exceed the 1 ng/L E2 equiv limit at Hirakata Bridge. When no river
252 biodegradation was assumed (Scenario 3), the PEC with 50th percentile river flow
253 changed little from the current condition. This phenomena reveals the density of STPs in
254 the river basin and relatively short flow time available for biodegradation. Applying the
255 ozonation tertiary treatment to all upstream STPs was predicted to more than halve the E1
256 concentrations compared to current conditions. The oxidation of organic micropollutants
257 by ozonation tertiary treatment has been reported to be an efficient process to improve the
258 removal efficiencies of the STPs²¹⁻²³. Looking at these modelling results, and given the
259 expense of ozonation one recommendation might be to use it only in winter when the
260 biological performance of STPs as at its weakest, and dilution lowest.

261

(Insert Figure 5)

262

263

264 **4 CONCLUSIONS**

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

277

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285

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336 **Figure Captions**

337

338 Figure 1 Yodo River basin, Japan.

339

340 Figure 2 Different scenarios examined in PEC estimations.

341

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

344

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

347

348 Figure 5 PEC of E1 and E2 equiv (in box) obtained from the model with 50th percentile
349 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 survey¹⁶

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

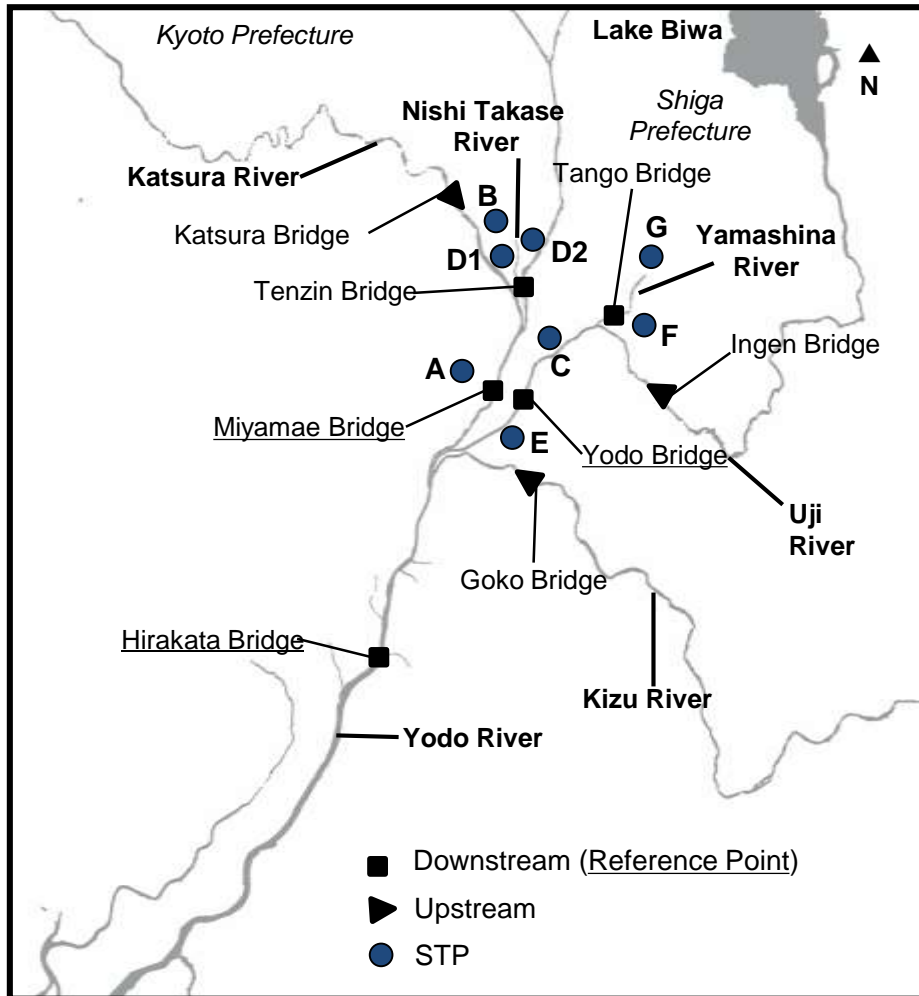


Figure 1 Yodo River basin, Japan.

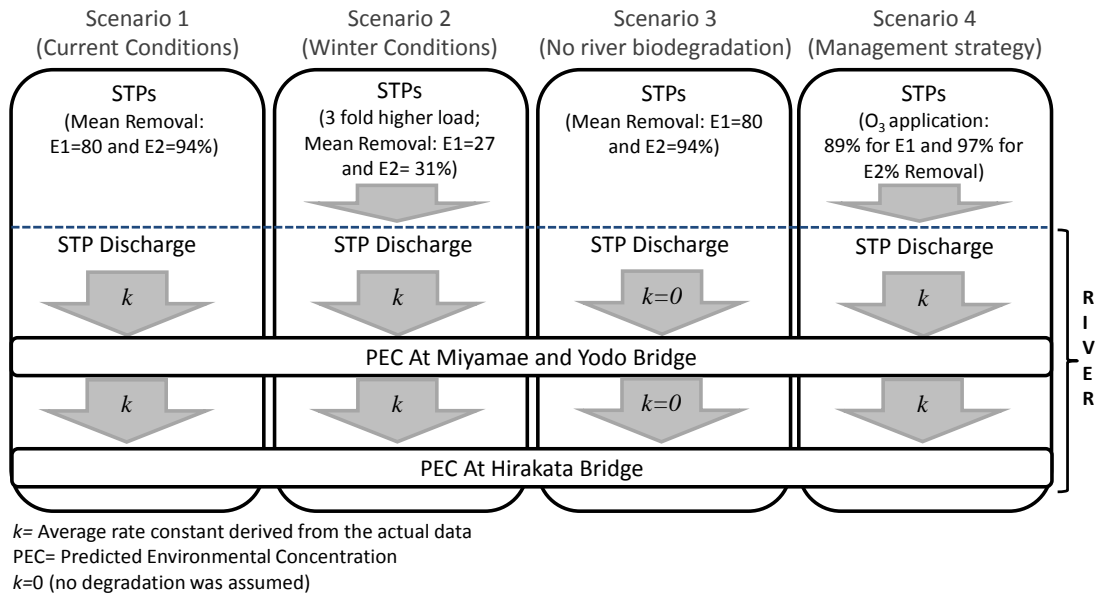
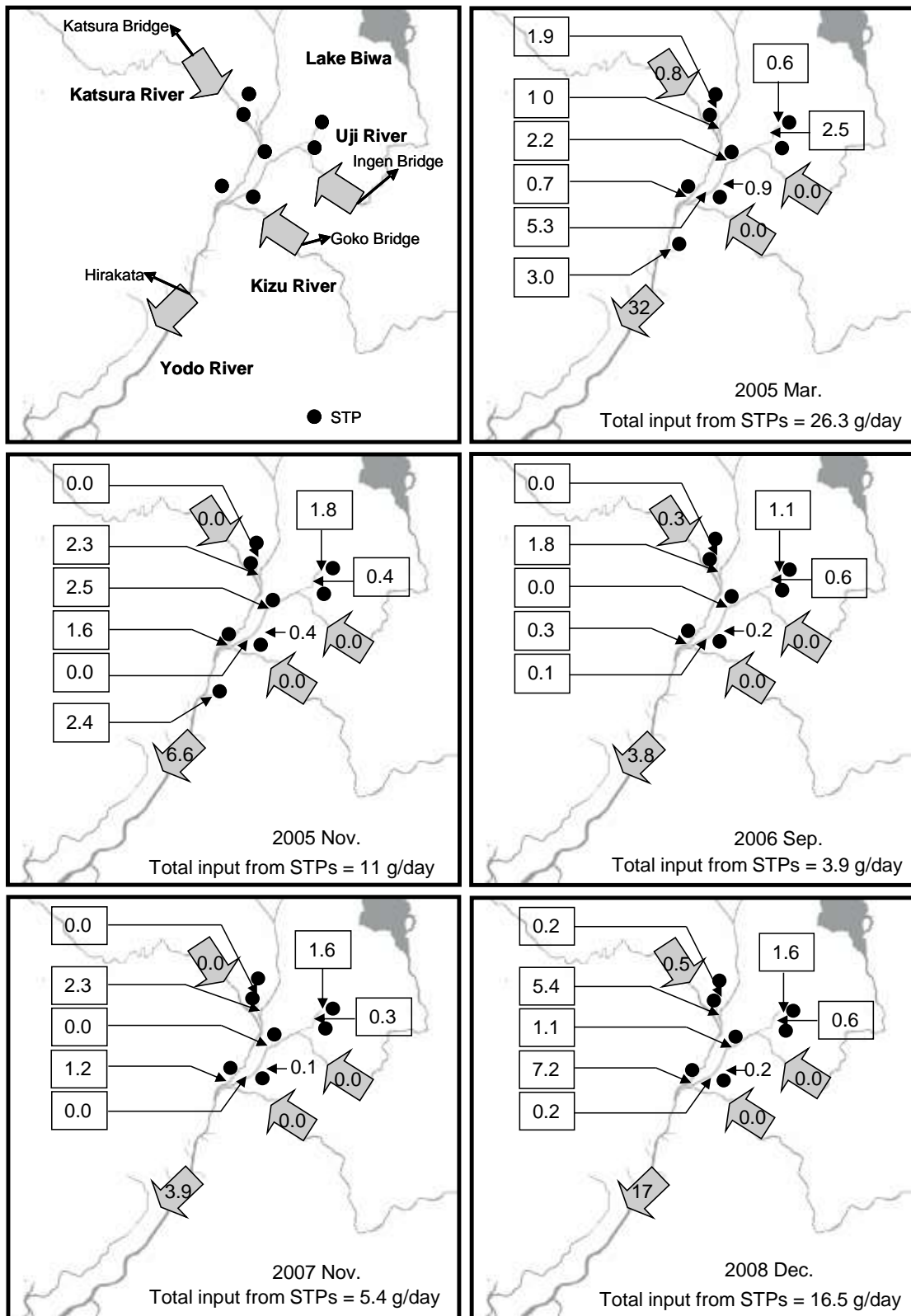


Figure 2 Different scenarios examined in PEC estimations.



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).

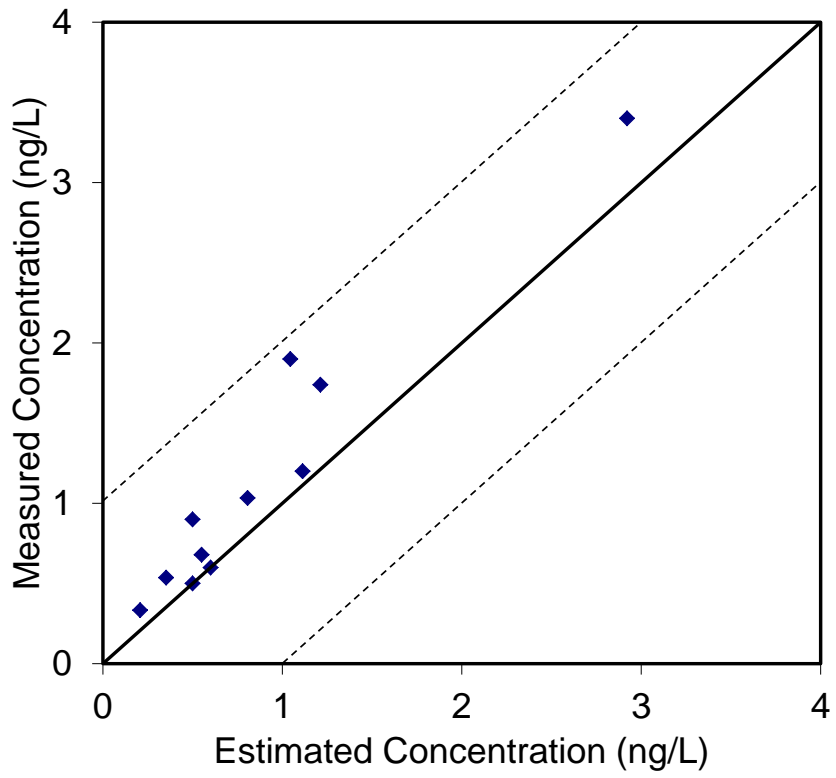


Figure 4 Comparison between the measured (dots) and estimated (lines) E1 concentrations obtained from the model at Miyamae, Yodo and Hirakata Bridge.

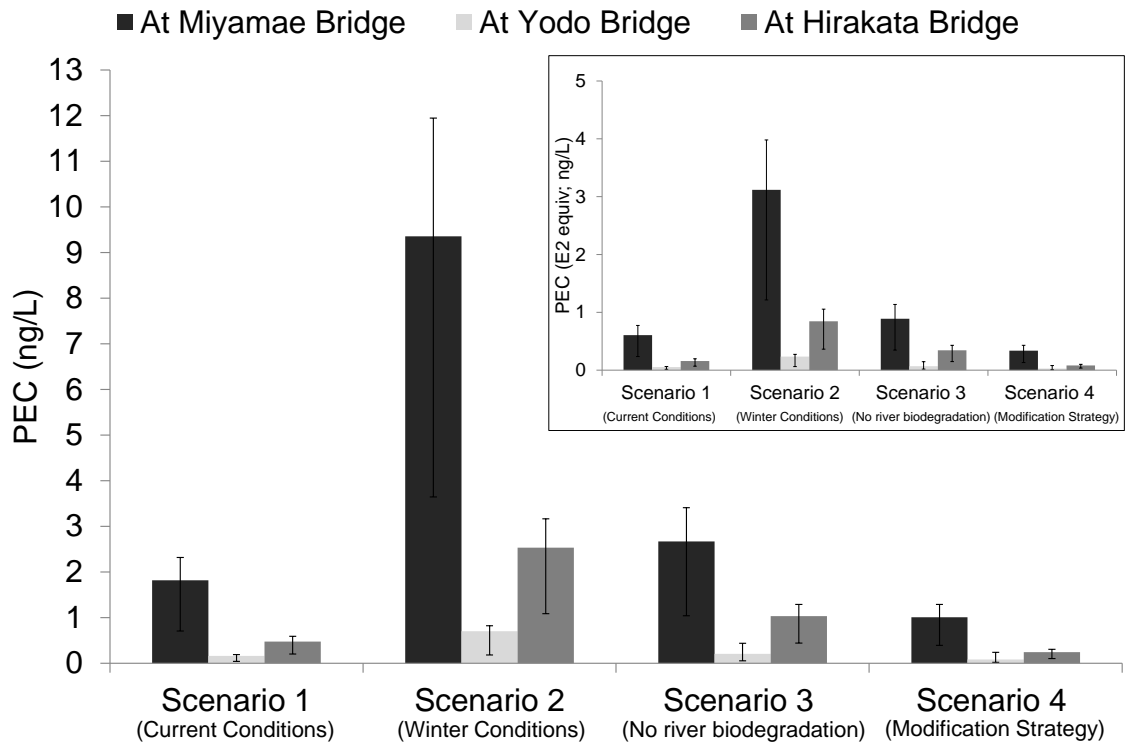


Figure 5 PEC of E1 and E2 equiv (in box) obtained from the model with 50th percentile flow (The error bars represent the 25th and 95th percentile PEC values).