Contemporary Engineering Sciences, Vol. 10, 2017, no. 7, 305 - 315
HIKARI Ltd, www.m-hikari.com
https://doi.org/10.12988/ces.2017.7116

Behavior of Toxicity in River Basins Dominated by Residential Areas

Riyanto Haribowo[1*], Minami Yoshimura[2], Masahiko Sekine[3], Tsuyoshi Imai[3], Koichi Yamamoto[3], Takaya Higuchi[3] and Ariyo Kanno[3]

[1] Department of Water Resources Engineering, Faculty of Engineering
Universitas Brawijaya, Malang, Indonesia

[2] Higashi Ward Offices, Hiroshima City Hall, Hiroshima, Japan

[3] Graduate School of Science and Technology for Innovation
Yamaguchi University, Tokiwadai, Ube, Yamaguchi, Japan

Abstract

River toxicity based on acute toxicity to Medaka fish and chemical concentrations measured using a gas chromatography–mass spectrometry simultaneous analysis database were investigated. Between June 2012 and January 2014, 21 samples were collected from three rivers in Japan that have most of their catchments in residential areas. Toxicity tends to remain stable even when the composition and concentration of chemicals fluctuate. Toxicity levels in a basin dominated by residential areas can be explained using a simple model with two parameters, k' (toxicity decrease ratio) and d_W (toxicity from effluents discharged by people without a sewer connection), which is commonly used for traditional organic pollution analysis. The estimated k' was 0.03 km^{-1}, and d_W was 0.08. However, when a sampling point is adjacent to commercial or industrial facilities, it becomes difficult to explain the lethal dilution rate (LDR_{50}) using this model. These findings suggest that water from residential areas sometimes has toxicity levels that are high enough to affect the aquatic habitat and these toxicity levels should be managed. Additionally, the pollution analysis procedure for sewerage design can be applied for toxicity management in rivers that have most of their catchments in residential areas.

[*]Corresponding author

Keywords: Aquatic habitat, Chemical concentration, Medaka fish, River toxicity, Residential area

1 Introduction

Toxicity is considered to be caused by various substances such as agricultural chemicals, detergents, and pharmaceuticals. Apart from these substances, trace chemicals such as endocrine disruptors and dioxins can cause many problems in the ecosystem, especially if released into water reservoirs in the environment [5, 9]. Studies have determined the acute toxicity levels of such chemicals. However, their concentrations in environmental water are usually much lower than the levels required to cause acute toxicity Medaka fish. Furthermore, various other chemicals are also present in the water. Therefore, it is difficult to obtain information that would be valuable for protecting the ecosystem from each of these chemicals.

A bioassay is one approach for obtaining comprehensive information about the toxicity levels of chemicals. However, this approach has been deemed unsuitable for environmental management because it cannot detect the chemical itself. As an alternative, toxicity management methods based on bioassays, such as Whole Effluent Toxicity, have attracted considerable attention in recent times. This method can be used to measure the toxicity of industrial wastewater itself, without necessarily identifying the chemical [12].

Separately, we have shown that a toxicity test using 100-fold concentrated river water and the Medaka fish can be used to detect acute toxicity in a river [14]. The toxicity tended to be higher when the biochemical oxygen demand was higher, even when there were no industries situated near the river. This implies that some toxicity may be attributable to household wastewater. Furthermore, we showed a relationship between toxicity and aquatic animal habitation. For example, the ratio of clear stream benthic animals sharply decreased in river waters in which 50% of the Medaka fish died within 4 h, and tolerant fish became dominant in waters in which 50% of the Medaka fish died within 3.3 h. This result shows that toxicity, an issue that cannot be ignored with regard to ecosystem conservation, is attributed to not only industries but also diffused pollutant sources such as residences.

In the field of environmental toxicology, there has been a great deal of research regarding the single toxicity of antibiotics on organisms over the last few decades, and most of the mechanisms of toxicity mostly have been determined [2, 10, 3]. Although many studies have focused on river water toxicity and chemical behaviors [4, 13], few studies have examined toxicity and chemicals in relation to basin characteristics in Japan. In this study, we investigated river water toxicity in three basins dominated by residential areas and identified the chemical contents using a gas chromatography–mass spectrometry (GC/MS) simultaneous analysis database [6].

2 Materials and methods

2.1. Study Area

Samples were taken from three rivers in Japan that have most of their catchment areas within residential areas. Fifteen grab samples (whole sample collected at one time) were collected from June to December 2012, and six composite samples (composed of subsamples collected at regular intervals over 24 h) were collected from August to January 2014.

The first sample area was located in river "M" (Figure 1). River "M" accommodates the flow of rainwater and household waste and has a residential area upstream. Five sampling sites along the river (M1, M4, M5, M6, and M7) were selected, and four sampling sites were selected from the tributary (M2, M3, M8, and M9). The second sample area was located in river "Y." The river basin is wide and the pollution risk is increased because the middle zone of the basin has rapidly urbanized over the past three decades. The third sample area was located in river "Z." The basin of this river includes one of the most densely populated cities in Japan. In addition, increasingly complex human social activities produce a wide range of chemicals in various concentration ranges. Therefore, it is very important to know the parameters that can affect water quality. Table 1 shows the spatial data for each river basin.

2.2. Acute Toxicity Test

Yamashita et al. [14] proposed a toxicity index that is the inverse of the median lethal time (LT_{50}^{-1}). Although it has an advantage in that a semi-quantitative index can be obtained using a smaller number of test fish, LT_{50}^{-1} also has a disadvantage, as it cannot be analyzed as a concentration. In this study, we needed an index that can be treated as a concentration. For this reason, we expressed toxicity as a lethal dilution ratio (LDR_{50}). LDR_{50} is the inverse of the lethal concentration ratio (LCR_{50}), which Liu et al. [8] proposed, and is defined as the dilution ratio at which 50% of fish survive the acute toxicity test.

For sampling water, 10 L river water was filtered through a 1-μm glass filter. Two sets of Sep-Pak® Plus PS-2 cartridges were set in series. Hydrophobic organic compounds were trapped at 10 mL/min for each 5 L sample of water and eluted from each cartridge in 10 mL acetone. Of the 40 mL of acetone solution generated, 36 mL was used for acute toxicity tests and 4 mL was used for GC/MS analysis. Acetone solution (36 mL) was evaporated to 200 μL under a purge of nitrogen gas. We have shown that 200 μL acetone (Wako Pure Chemical Industries, Ltd, product number 015-11281) diluted to 50 mL has no acute toxicity effect on Medaka fish. The acetone solution was diluted to 90 mL, and then 10, 20, 50, and 100-fold dilutions were prepared, using 5, 20, 25, and 50 mL of solution, respectively, diluted with the appropriate volume of water. All dilution steps used water dechlorinated with activated carbon.

In the toxicity test based on Liu et al. [7], the lethal effect was observed by exposing groups of 10 larval Medaka (48–72 h old) to 25 mL of each solution for 48 h. Each dilution was tested in duplicate, and when there was a striking difference in test results between duplicates, the test was considered a failure. Toxicity was analyzed using the Probit method. The reliable range of LDR_{50} depends on the concentration steps used, and the value was between 0.01 and 0.2 in this study.

Table 1. Spatial data for each river basin

Date	Sampling point	LT_{50}^{-1}	LDR_{50}	Temp. (°C)	Catchment area (km^2)	Farmland area (km^2)	Commercial area (km^2)	Industrial area (km^2)	Sewer population (people)
2012-12-14	M1	>2.00	0.067	10.9	1.75	0.01	0.05	0.00	1
2012-12-14	M2	>2.00	>0.2.000	10.9	0.06	0.00	0.01	0.00	0
2012-12-14	M3	>2.00	0.086	10.7	1.99	0.17	0.25	0.00	154
2012-10-31	M4	0.33	0.019	17.1	3.81	0.18	0.52	0.00	249
2012-10-31	M5	0.01	0.020	17.1	3.88	0.18	0.52	0.00	916
2012-06-16	M6	0.01	0.011	23.1	4.08	0.18	0.52	0.00	1026
2012-06-16	M7	0.05	0.014	23.3	4.21	0.21	0.52	0.00	1654
2012-06-16	M8	0.019	0.019	23.6	0.09	0.03	0.02	0.00	600
2012-06-16	M9	>2.00	>0.2.000	23.6	0.04	0.00	0.03	0.00	28
2012-11-23	Y1	0.06	0.016	12.0	6.52	0.63	1.05	0.00	17411
2012-11-23	Y2	0.05	0.016	12.0	6.52	0.63	0.80	0.00	17411
2012-09-23	Y3	0.09	0.039	22.8	6.52	0.63	0.80	0.00	17411
2012-09-23	Y4	0.09	0.022	22.7	4.40	0.08	1.47	0.00	20352
2013-08-20	Y4c1	0.03	0.011	30.9	4.40	0.08	1.47	0.00	20352
2013-10-21	Y4c2	0.02	0.010	20.2	4.40	0.08	1.47	0.00	20352
2014-01-08	Y4c3	0.20	0.016	6.5	4.40	0.08	1.47	0.00	20352
2012-09-23	Y5	0.02	0.011	22.7	69.90	6.80	5.75	0.17	206025
2013-08-20	Y5c1	0.02	0.011	31.2	69.90	6.80	5.75	0.17	206025
2013-10-21	Y5c2	0.00	0.010	19.2	69.90	6.80	5.75	0.17	206025
2014-01-08	Y5c3	0.01	0.000	6.5	69.90	6.80	5.75	0.17	206025
2012-09-22	Z	0.07	0.019	28.2	59.47	11.82	4.02	0.17	183604

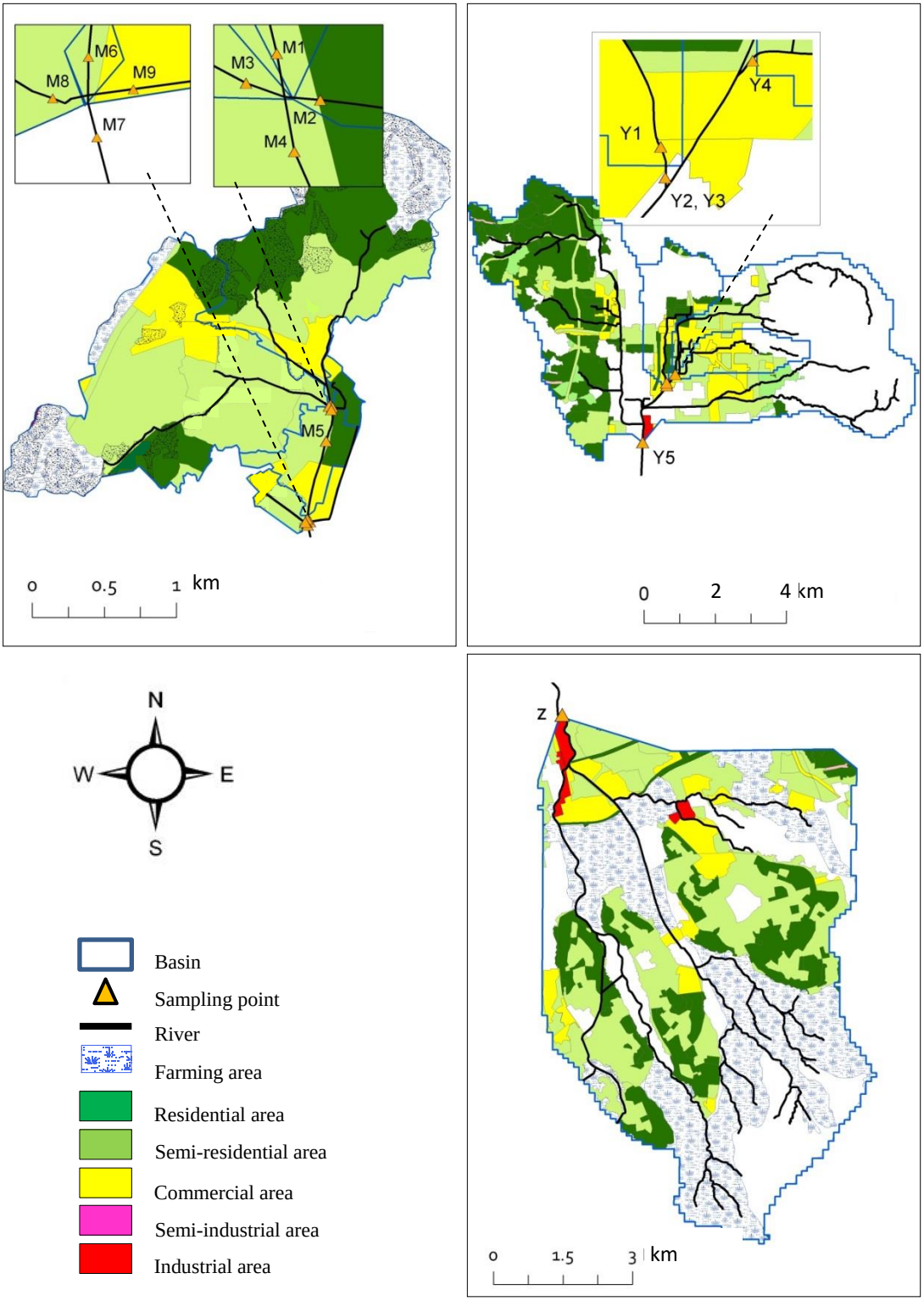

Fig. 1. Basin areas of rivers “M,” “Y,” and “Z.”

2.3. Cluster Analysis

To investigate the similarity of chemical substances among water sampling sites, cluster analysis was used. When the degree of dispersion of the data is unknown, it is difficult to choose the clustering method theoretically, and a trial and error approach is needed. In this study, Ward's method, the group average linkage method, the centroid method, and the complete linkage method were used for clustering, and Euclidean distance and squared Euclidean distance were used as measures of the subjects' distance. Statistical analysis was performed using SPSS version 20. Only the results of Ward's method are presented here.

2.4. Formulation of Toxicity Runoff Process

The decay of substances is frequently modeled as a first-order reaction; that is, assuming that the decay rate of the substance is proportional to the amount of substance present. The decomposition rate is calculated based on the first-order kinetics reaction

$$C_t = C_0 . e^{-kt} \tag{1}$$

Here, C_t = concentration remaining at time t, C_0 = initial concentration, k = ratio of pollutant decrease, and t = time elapsed. In practice, estimating the flow time of rivers is difficult. Therefore, time elapsed was replaced with flow-down distance [11].

$$C = C_0 \times e^{-k' x} \tag{2}$$

We assumed that the maximum flow-down distance is proportional to the square root of the basin area. Since LDR_{50} can be treated as a concentration, the concentration at the basin exit becomes:

$$C = \frac{C_0}{\sqrt{B}} \int_0^{\sqrt{B}} e^{-k' x} dx \tag{3}$$

Then equation (3) becomes:

$$C = \frac{C_0}{k' \times \sqrt{B}} \times \left(1 - e^{-k' \sqrt{B}}\right) \tag{4}$$

Here, C = LDR_{50} in a basin outlet (-), B = basin area (km^2), and k′ = ratio of toxicity decrease (km^{-1}).

We assumed that factors such as population, farming, industrial activity, and sewerage conditions contribute to discharge of toxic substances, and that C_0 is expressed by a linear combination of these elements as follows:

$$C_0 = \sum_{i=1}^{n} d_i \times F_i \tag{5}$$

Here, d_i = unit loading ratio (-), F_i = percentage of frame values (-), i = spatial category. In this study, i = {F, C, I, S, W}, where F represents farmland

area, C represents commercial area, I represents industrial area, S represents a population with a sewer connection, and W represents a population without a sewer connection. For example, F_W represents the proportion of people that do not have a sewer connection and d_W represents LDR_{50} from effluents discharged by people without a sewer connection.

The toxicity runoff process is also affected by the minimum winter temperature. The toxicity decrease ratio can be estimated at any other temperature by using:

$$k' = k'' \times \theta^{T-20} \tag{6}$$

Here, k'' = ratio of toxicity decrease (km^{-1}) at 20°C, T = temperature (°C). The value of θ generally used for domestic sewage is 1.035 [1]. Combining Eqs.4, 5, and 6, C is expressed as:

$$C = \frac{\sum d_i \times F_i}{k'' \times 1.035^{T-20} \times \sqrt{B}} \times \left(1 - e^{-k'' \times 1.035^{T-20} \times \sqrt{B}}\right) \tag{7}$$

Since values of B, F_i, T, and C are known through our surveys, we should be able to determine k' and d_i by minimizing the squared error between the calculated and observed C by using a nonlinear optimization technique, if the model represents the toxicity runoff process properly. For optimization, we used the Generalized Reduced Gradient Nonlinear Solving Method implemented in Solver add-in of Microsoft Excel 2010.

3 Results and discussion

3.1. Detection of Toxicity

Originally, LDR_{50} analysis involved observation only at the 48th [7]; however, in this study, we noted observations at 0.5, 1, 2, 3, 6, 12, 24, and 48 h. Therefore, we can also obtain LT_{50}^{-1}. In our previous study using Medaka fish and 100-fold concentrated water to detect the toxicity level that affects the aquatic habitat, the ratio of benthic animals sharply decreased when LT_{50}^{-1} was over 0.25, and tolerant fish became dominant at LT_{50}^{-1} over 0.3 [14]. In this study, LT_{50}^{-1} for M2, M9, M1, and M3 were all over 2.0. The reliable range for LT_{50}^{-1} is between 0.02 and 2.0 [14]. These results show that water from residential areas sometimes has toxicity levels that are high enough to affect the aquatic habitat, and these toxicity levels should be managed.

3.2. Chemical Concentration and Grouping of Sampling Points based on Cluster Analysis

Figure 2 shows the results of the cluster analyses. Distance indicates the similarity of chemical substances among water sampling sites; a smaller distance indicates stronger similarity. We chose a distance of 15 as the classification threshold because this produced clear grouping results. By synthesizing the results of the two cluster analyses, we identified seven groups. The sites included in Group 1

were Z, M3, Y1, M1, Y3, Y4, and Y5. Euclidian distances also placed M2 and M4 in the same cluster, while squared Euclidean distances separated them. However, since M2 and M4 remained together in one cluster, they formed Group 2. M5 was placed in Group 3, and M6 was placed in Group 4, since Euclidian distances placed them in the same group, while squared Euclidean distance separated them. M7 and M8 formed Group 5, M9 formed Group 6, and Y2 formed Group 7.

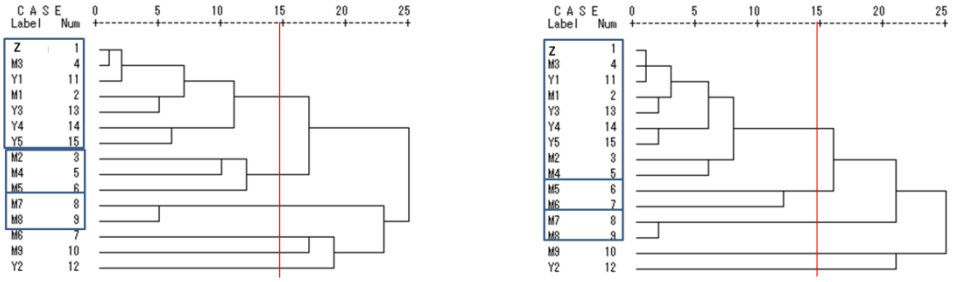

Fig. 2. Classification based on Ward's method using Euclidian distances (left) and squared Euclidean distance (right)

Table 2 shows the chemical concentrations from the GC/MS analysis arranged according to the cluster analysis results. In Group 1, the chemical composition differed from basin to basin, and almost all substances were present at low concentrations. High toxicity does not always involve high chemical concentrations. For example, compared with other sample points, M3 had the highest toxicity value (0.086), but all the chemical concentrations were low. There are several possible reasons for this inconsistency, such as the difficulty of detecting all chemicals or a synergistic effect of the chemicals. Thus, it is difficult to prove an apparent relationship between toxicity and chemical concentrations using these methods.

In Group 2 (M2 and M4), various chemicals (e.g., 2-phenoxyethanol, found in hair care products and perfumes) were present in high concentrations. Sampling point M2 is surrounded by commercial facilities, while M4 is downstream of M2 and directly adjacent to commercial facilities. These locations are likely to explain the high chemical concentrations. The conditions in Group 2 are similar to those in Groups 4 and 7, which also have sampling points adjacent to commercial or industrial facilities and have high concentrations of some chemicals.

Sample from M5 (Group 3) were collected on the same day as M4, specifically to determine the decrease ratio. For many chemicals, the concentration increased from M4 to M5, and several chemicals were not detected in M4 but appeared in M5. The composition and concentration of chemicals fluctuated too. However, toxicity tends to remain stable even when the composition and concentration of the chemicals fluctuate.

M6 (Group 4) was located downstream from M5. Since M6 is located near commercial areas, these might be the sources of high chemical concentration. M7 and M8 formed Group 5, and both sites had low chemical concentrations, as in

Group 1, except for bromobutide (a herbicide). Streams from M6, M8, and M9 mix and flow to M7. Therefore, a herbicide used in a farming area of the small M8 basin was also detected at M7. This showed that, especially in small basins, high chemical concentrations might be found as a result of irregular events such as spraying of herbicides.

M9, which differed from the other sampling points, formed Group 6. M9 was unique in that it contained mostly commercial areas and had high chemical concentrations and toxicity. Although Group 1 had no characteristic land use composition, it can be said that the sampling points of Group 1 were not adjacent to commercial and/or industrial facilities.

3.3. Outflow Mechanism of Toxicity in River Basins

Although we tried to determine k and d_i in equation (7), using data from all sampling points, the observed and calculated C did not show a clear relationship. Furthermore, unit loading ratio values from farmland area, commercial area, industrial area, and population with a sewer connection showed 0 values, which indicates that toxic substances were not released from those areas. Therefore, by using only data from the Group 1 sampling points (which were not adjacent to commercial facilities) and setting $d_i = 0$ for all except d_W, we obtained a linear relationship between observed and calculated C (Figure 3). This means that toxicity from the Group 1 basin can be explained using equation (7) with only two parameters, k′ (toxicity decrease ratio) and d_W (toxicity from effluents discharged by people without sewer connection). The obtained k′ was 0.03/km, and d_W was 0.08.

As shown in Figure 3, sampling points not included in Group 1 did not fit equation (7). When a sampling point is adjacent to commercial or industrial facilities, a simple model like equation (7) cannot explain LDR_{50}. However, sometimes a sampling point adjacent to commercial or industrial facilities did fit this model equation, like Y2 and M8. This might imply that, in river basins dominated by residential areas, even when commercial or industrial facilities discharge specific chemicals, they do not remain for very long in the stream, and chemicals discharged from residences tend to dominate.

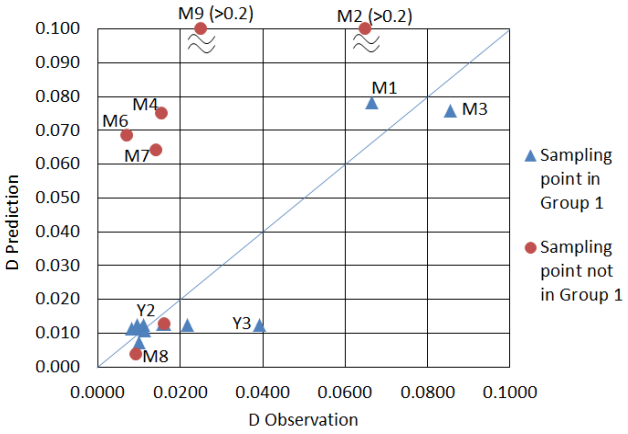

Fig. 3. Relationship between observed and calculated toxicity.

4 Conclusions

Toxicity discharged from a basin dominated by residential areas can be explained using a simple model with two parameters, k′ (toxicity decrease ratio) and d_W (toxicity from effluents discharged by people without a sewer connection), which is commonly used for traditional organic pollution analysis. The obtained k′ was 0.03 km^{-1}, and d_W was 0.08. However, when a sampling point is adjacent to commercial or industrial facilities, it becomes difficult to explain lethal dilution rate (LDR_{50}) using this model. Finally, these findings suggest that water from residential areas is, sometimes toxic enough to affect the aquatic habitat, and these toxicity levels should be managed. The pollution analysis procedure for sewerage design can be applied for toxicity management in rivers that have most of their catchments in residential areas.

Acknowledgements. The authors are grateful to Katsumasa Tanaka and Yoshihiro Shimono from Yamaguchi Prefectural Institute of Public Health and Environment for their kind assistance and valuable advice throughout the study.

References

[1] S.J. Arceivala, S.R. Asolekar, *Wastewater Treatment for Pollution Control and Reuse*, Tata McGraw-Hill Professional, 2009.

[2] T. Backhaus, M. Scholze, L.H. Grimme, The single substance and mixture toxicity of quinolones to the bioluminescent bacterium Vibrio fischeri, *Aquat. Toxicol.*, **49** (2000), 49-61. https://doi.org/10.1016/s0166-445x(99)00069-7

[3] M. Gonzalez-Pleiter, S. Gonzalo, I. Rodea-Palomares, F. Leganes, R. Rosal, K. Boltes, E. Marco, F. Fernandez-Pinas, Toxicity of five antibiotics and their mixtures towards photosynthetic aquatic organisms: implications for environmental risk assessment, *Water Res.*, **47** (2013), 2050-2064. https://doi.org/10.1016/j.watres.2013.01.020

[4] I. Ichiki, V. Mixay, Urban runoff pollutant characteristics in Vientiane capital, Lao PDR, *J. Water Environ. Tech.*, **7** (2009), no. 3, 177-185. https://doi.org/10.2965/jwet.2009.177

[5] B. Jimenez, Environmental effects of endocrine disruptors and current methodologies for assessing wildlife health effects, *Trends Anal. Chem.*, **16** (1997), no. 10, 596-606. https://doi.org/10.1016/s0165-9936(97)00098-8

[6] K. Kadokami, K. Tanada, K. Taneda, K. Nakagawa, Novel gas chromatography–mass spectrometry database for automatic identification and quantification of micropollutants, *J. Chromatogr.*, **1089** (2005), 219-226.

https://doi.org/10.1016/j.chroma.2005.06.052

[7] R. Liu, T. Kameya, A. Sawai, K. Urano, Application of a larval Medaka assay to evaluate the fish safety level in Sagami River, Japan, *Environ. Monit. Assess*, **130** (2007), 475-482. https://doi.org/10.1007/s10661-006-9437-9

[8] R. Liu, T. Kameya, Y. Sugimura, A. Sawai, T. Shigeoka, K. Urano, A larval medaka (Oryzias latipes) acute toxicity assay combined with solid-phase extraction to efficiently determine the toxicity of organic contaminants in river water, *Water Sci. Technol.*, **53** (2006), no. 11, 213-219. https://doi.org/10.2166/wst.2006.355

[9] M. Murata, N. Iseki, S. Masunaga, J. Nakanishi, Estimation of effects of dioxins and dioxin-like PCBs on wildlife population—a case study on common cormorant, *Chemosphere*, **53** (2003), 337-345. https://doi.org/10.1016/s0045-6535(03)00008-0

[10] C.M. Oliphant, G.M. Green, Quinolones: a comprehensive review, *Am. Fam. Physician*, **65** (2002), 455-465.

[11] M. Sekine, *Systematic Pollutegraph Simulation for Real Scale River*, PhD Thesis, Department of Engineering, Kyoto University (in Japanese), 1991.

[12] M. Tonkes, P. De Graaf, J. Graansma, Assessment of complex industrial effluents in the Netherlands using a whole effluent toxicity (or wet) approach, *Water Sci. Technol*., **39** (1999), no. 10-11, 55-61. https://doi.org/10.1016/s0273-1223(99)00253-x

[13] Wang L, Ying G, Zhao J, Liu S, Yang B, Zhou L, Tao R, Su H, Assessing estrogenic activity in surface water and sediment of the Liao River system in northeast China using combined chemical and biological tools, *J. Environ Pollut*., **159** (2011), 148-156. https://doi.org/10.1016/j.envpol.2010.09.017

[14] H. Yamashita, R. Haribowo, M. Sekine, N. Oda, A. Kanno, Y. Shimono, W. Shitao, T. Higuchi, T. Imai, K. Yamamoto, Toxicity test using medaka (Oryzias latipes) early fry and concentrated sample water as an index of aquatic habitat condition, *Environ. Sci. Pollut. Res*., **19** (2012), no. 7, 2581-2594. https://doi.org/10.1007/s11356-012-0906-0

Received: February 15, 2017; Published: March 2, 2017