The characteristics and measuring technique of refractory dissolved organic substances in urban runoff

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Abstract It is considered that refractory dissolved organic substances have caused an increase in the COD concentration in Lake Biwa in recent years. We investigated the organic matter in the first flush of stormwater runoff from a road in the watershed area of the lake, and studied the possibility of improvement in the water environment from that aspect. After percolating the stormwater through soil, we analyzed organic substances fractionated by using GPC-TC. And we examined the effect of removal of organic substances by comparing the peak height before and after percolation. In the result of the experiments, we found that soil infiltration reduced the refractory dissolved organic substance and we successfully designed a system for a simple and easy experimental facility to treat urban runoff.

Keywords First flush runoff; GPC-TC analysis; organic substance; refractory; soil; stormwater runoff

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Introduction

In the Lake Biwa Basin, they have implemented a system for total effluent control and water quality management for point source pollution. The water quality of Lake Biwa has had a decreasing BOD concentration since 1984, but it has an increasing COD concentration (Shiga pref., 2001). We call it the divergent phenomenon of BOD and COD (Figure 1). In regard to the divergence of the COD and the BOD concentration, it is considered that refractory dissolved organic substances cause the increase in the COD not the BOD. This substance may increase the amount of organic substance which cannot be decomposed by microorganisms (Imai *et al.*, 1998; Yonebayashi, 2004). Additionally, the water quality that flows into Lake Biwa from the rivers doesn't progress in terms of improvement, because the COD concentration remains unchanged or increases under the aging phenomena. As for the cause of the increase of COD, it is implied from the study that there is a possibility of significant influence of the catchment area.

However, the catchment basin of Lake Biwa has undergone rapid urban development in recent years, and impervious land surface has increased. In the result, we can't disregard the non-point source pollution from urban runoff as a significant influence on the water environment of Lake Biwa. So it's imperative that we have to take effective action against the non-point source pollution from the impervious surfaces such as the buildings and the roads, because the sediment deposited in those areas is discharged into the river and channels along with the urban runoff at a time (Barrett *et al.*, 1998; Great Lakes Science Advisory Board, 2000).

The aim of this study is to reduce non-point pollution sources from the urban area. In this paper we discuss refractory dissolved organic substances that we investigated and their characteristics within the urban runoff. Finally we put forward a proposal on effective means to reduce the pollutant load.

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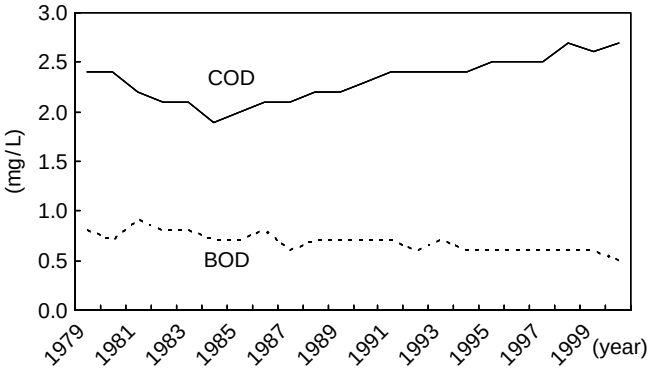

Figure 1 Divergent phenomenon of BOD and COD concentration of Northern Lake Biwa

Methodology

The characteristics of urban runoff

The site used is situated on the southeast area of Lake Biwa which is the lakeshore road in Kusatsu City. The road usually carries 12,000 vehicles per 12 hours (Shiga Pref., 1999). This area from which runoff is collected is assumed to be a parallelogram of approximately 750 m^2. We investigated the characteristics and dynamics of stormwater runoff from this road surface. The runoff was collected over time intervals during one rainfall. We analyzed the samples collected using the method outlined below.

Gel Permeation Chromatography - Total Carbon Analysis (GPC-TC Analysis). The sample is filtrated using a 0.45 μm membrane-filter, and the filtrate is evaporated at 10–60 times using freeze concentration. The measured amount of this sample and the solution were injected into the GPC-TC analysis. The operating conditions for GPC-TC are presented in Table 1, and these conditions were established in accordance with those by Yonebayashi (1995), Higashi *et al.* (1997) and Shiga Pref. Report (1997). GPC-TC chromatogram is shown as the organic volume and peaks of higher molecular weight substances appear at an earlier stage of the chromatogram. The most delayed peak, (3) shown in Figure 2, is the inorganic dissolved carbon, and according to the report, the water of Lake Biwa has a peak at retention time of around 50 min (1) and three peaks at retention times from 70 to 80 min (2); (1) including the products by photosynthesis is biodegradable. However, (2) is said to include refractory dissolved organic substances because it remains after the biodegradable test (Figure 2).

Biodegradable test (Fukushima et al., 1995, 1996, 1997). A road runoff sample batch was placed into a 5,000 ml brown glass container, and the bottle was sealed using sterile silicon. Next the bottle was placed into a centrifuge at a moderate speed. This machinery was covered with sheets to shut out the light completely. The sample was then kept for

Table 1 Analytical conditions of GPC-TC

	Measuring condition
Column	Asahipak GS-320 (50 cm)
Mobile phase	30 mmol L^{-1}-Na_2HPO_4 (pH 6.0)
Flow rate	1.5 mL/min
Injection volume	1 mL
Detector	Total carbon analyzer

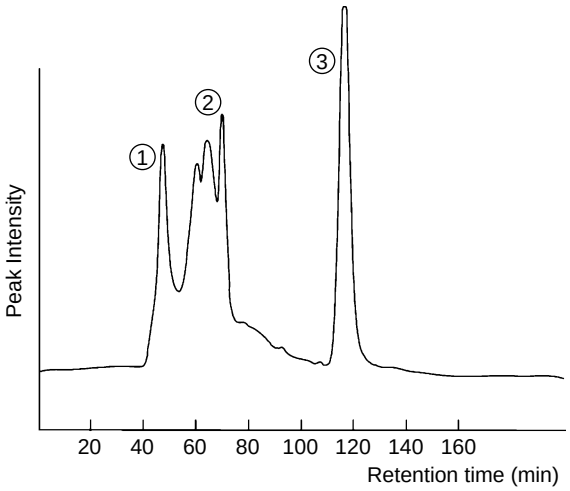

Figure 2 GPC-TC chromatogram; numerals in the circle indicate main three peaks

one hundred days with a water temperature set at 20°C. The sample then underwent a biodegradable test. Each sample was tested before the biodegradable test and one hundred days after the biodegradable test, these samples were analyzed for TOC and organic substances and fractionated using GPC-TC.

Field experiment for water purification

As the technique reducing pollutants in the first flush runoff from the road surface, we have taken the soil into consideration. In our previous research and papers, we stated that the soil has mechanisms that are physical, chemical and biological. And these mechanisms have proven to be effective in reducing various pollutants, especially phosphorus and D-COD (Tomioka *et al.*, 1988; Wada *et al.*, 2001). According to their reports, the soil had capacity to absorb the D-COD for three years in purifying the lake water.

So, we have conducted a field experiment with the intention of looking at the first flush pollutants in the stormwater runoff from the road surface and then studied effective techniques in reducing pollutants by using the capacity of the soil. The experiment site is the Kunobe overbridge of the Kibe-Yasu Line in Yasu Shiga prefecture.

Stormwater runoff from the road is transferred from the drainage area to the experimental facility (Figure 3) under the bridge. This facility is designed to selectively collect the first flush runoff and to percolate it through soil, based on the foregoing and other study results (Shiga pref. report, 2000). We used a decomposed granite soil that is low cost and a good capability of water purification.

Stormwater runoff was sampled four times during the experimental period (September 14, 2001–January 17, 2002) on Kunobe overbridge. The samples collected are the first flush runoff and treated effluent through the system filled with the soil, and these samples were then analyzed.

Results and discussion

The characteristics of urban runoff

Organic substances in stormwater runoff from the road. At the lakeshore road in Kusatsu City, we collected samples for 0–15 minutes where the starting flush (drainage volume of runoff was 185 l, catchment area was 750 m^2, equivalent to about 2 mm rainfall), and used the biodegradable test. In the result, the TOC concentration remained

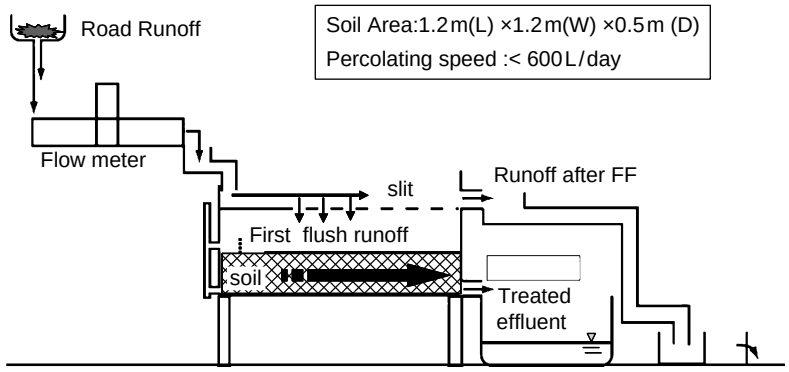

Figure 3 Schematic diagram of the experimental facility (Arrows indicate the stream of water)

at approximately 80% in the first flush runoff. And the DOC concentration remained at 50%; the POC concentration remained at 90%.

The GPC-TC chromatograms of before the biodegradable test and one hundred days after the biodegradable test are presented in Figure 4. The peak at approximately 50 minutes of the retention time indicates clearly that decomposable organic substances disappear after one hundred days, but the peak of 70 to 80 minutes shows that the refractory organic substances have a much smaller rate of decrease. Consequently the first flush runoff includes refractory organic substances and this suggests that it is the main pollutant load found in the water environment.

Characteristics of runoff from road surface. We conducted a survey seven times to measure the characteristics of the stormwater runoff during January 1999–September 2000. We collected the samples from the barrow pit at certain times and analyzed organic substance concentration.

The relationship between the COD and the TOC concentration of the stormwater runoff are presented in Figure 5. They show a strong correlation between the COD and the TOC concentration ($y = 1.0286x - 1.5673$; $R^2 = 0.9876$). Therefore, in this study we see no problem regarding the COD concentration in relation to the organic substances shown in the GPC-TC chromatogram.

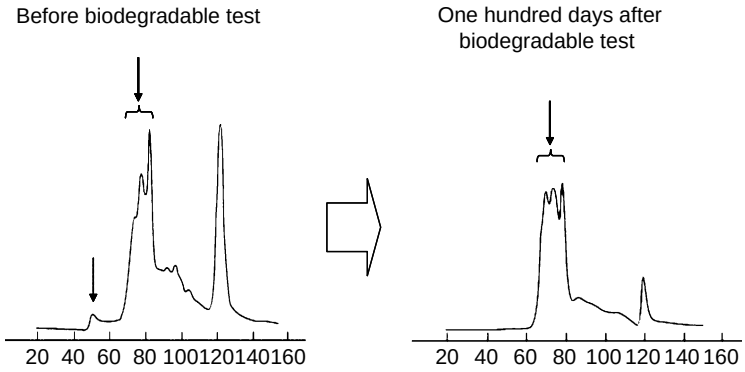

Figure 4 Biodegradable test of road runoff (24 Jan. 1999: Sinhayama Bridge Road in Kusatsu). Arrows indicate significant peaks

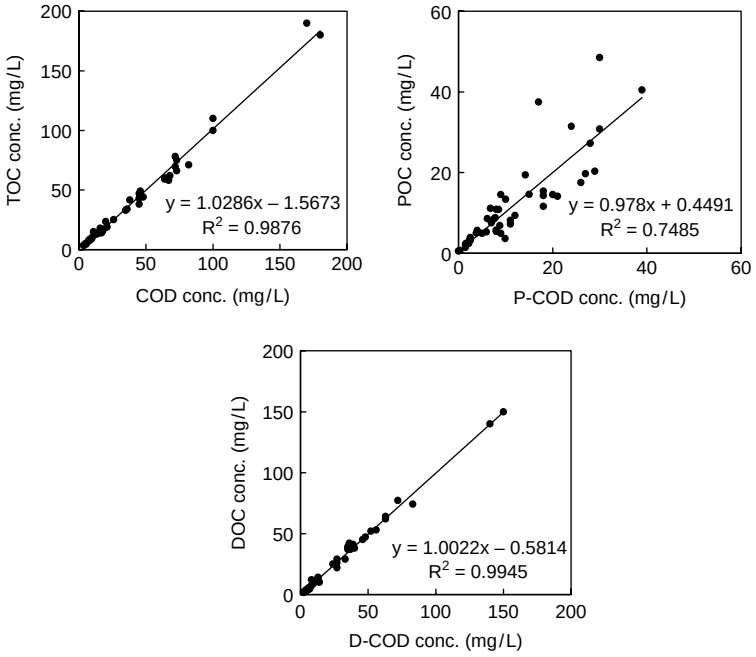

Figure 5 Relationship between COD and TOC concentration

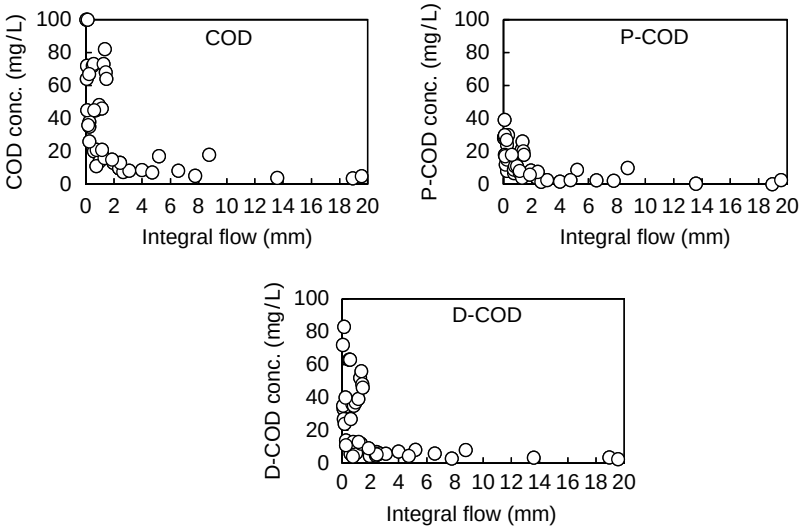

Figure 6 Relationship between COD and integral flow

Next, it is important to look at the relationship between the COD concentration of the stormwater runoff and integral flow shown in Figure 6. It is commonly known as a major pollutant of stormwater runoff during the time of the immediate flush. These surveys show the same tendency. Moreover there is a very strong relationship between dissolved organics i.e. D-COD and DOC. There is a possibility that the COD concentration of the first flush runoff exceeds five times that of the outflow drainage after the first flush when the concentration values are compared. As characteristics of the runoff from the road surface, we confirmed that a high concentration of pollutant continued until approximately 2.0 mm of integral flow.

Table 2 Characteristics of site in experiments

Location	Type	ADT* Vehicles/12 h	Surface type
Kunobe overbridge (Kibe-Yasu Line in Yasu)	Urban	11,966 (Compact vchicles) 1,036 (Heavy vehicles)	Asphalt

*Average daily traffic

Table 3 Summary of the observed rainfall

Data	Catchment area (m^2)	Days to rain (day)	Rainfall (mm)	Period of raining (h)	Drainage volume of runoff (mm)	Volume of treated runoff (mm)
30 Sep. 2001	285	2.1	11.0	9.7	9.5	3.4
16 Oct. 2001	285	3.2	5.0	7.0	3.8	2.7
03 Nov. 2001	285	5.6	13.0	9.8	9.8	3.8
29 Nov. 2001	285	17.5	11.0	10.4	5.7	3.2

Judging from the results of this survey, the stormwater runoff from the road surface includes refractory dissolved organic substances, and the organic substance contained in the first flush runoff is of a high concentration. It is, therefore, necessary to reduce the runoff pollutant loadings from the road surface in order to reduce the COD concentration. Considering the measures to reduce non-point source pollution, we can carry out these measures effectively and efficiently by implementing solutions to cover outflow drainage from the starting flush to 2.0 mm of integral flow.

Field experiment for water purification

Results of the water quality survey. Characteristics of experiment sites conducted under the Kunobe overbridge in Yasu and the summary of observed rainfall in the form of a survey are presented in Tables 2 and 3. As the volume of treated runoff is close to the first flush of 2.0 mm, we confirmed that this system is a selective intake of the first flush runoff.

COD concentration of the monitoring in four rainfalls is shown in Figure 7, and concentrations of COD components accumulated in the samples are shown in Figure 8.

The COD concentration of the first flush runoff is 2–4 times higher than that found in the runoff after the first flush, and is 4–6 times higher than that found in the treated effluent. Runoff after the first flush is the same or about two times higher than that of the treated effluent. So we have been able to effectively reduce the pollution in the first flush runoff. Additionally, the first flush runoff has a high proportion of particle species and accounts for approximately 50% of all particles found.

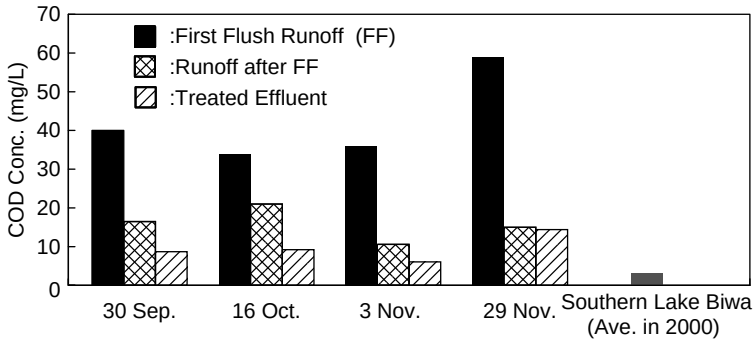

Figure 7 COD concentration of the monitoring

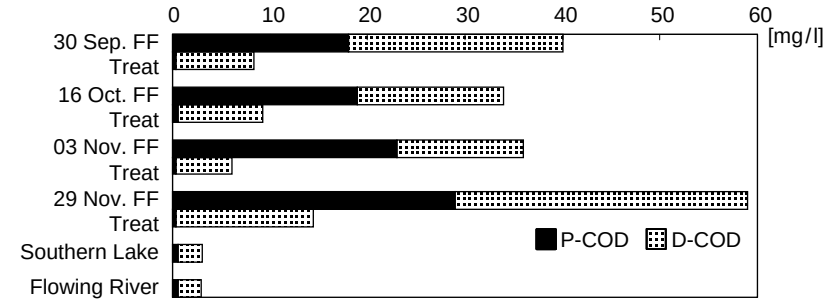

Figure 8 Concentration of COD components accumulated in the samples (FF: First Flush Runoff)

As the removal ratio of P-COD is more than 95%, the P-COD concentration can be reduced to several percent by percolating the runoff through the soil. Moreover, the P-COD concentration of the treated effluent is similar to the water quality of Lake Biwa and rivers flowing into Lake Biwa. The removal ratio of the monitoring is COD 77.5%, P-COD 97.7%, and D-COD 53.7%.

According to the results, we can reduce the first flush runoff loading by about 4–6 times using the methods in this experiment, though the COD concentration of the first flush is high compared with that of Lake Biwa and the rivers flowing into Lake Biwa.

GPC-TC chromatograms. The GPC-TC chromatograms of the first flush runoff and the treated effluent of each experiment are shown in Figure 9. For all of the survey, the peak intensity of GPC-TC chromatogram of the treated effluent in total retention times (for 50–120 minutes) was low. Both the easily decomposable dissolved organic substances and the refractory dissolved organic substances were reduced.

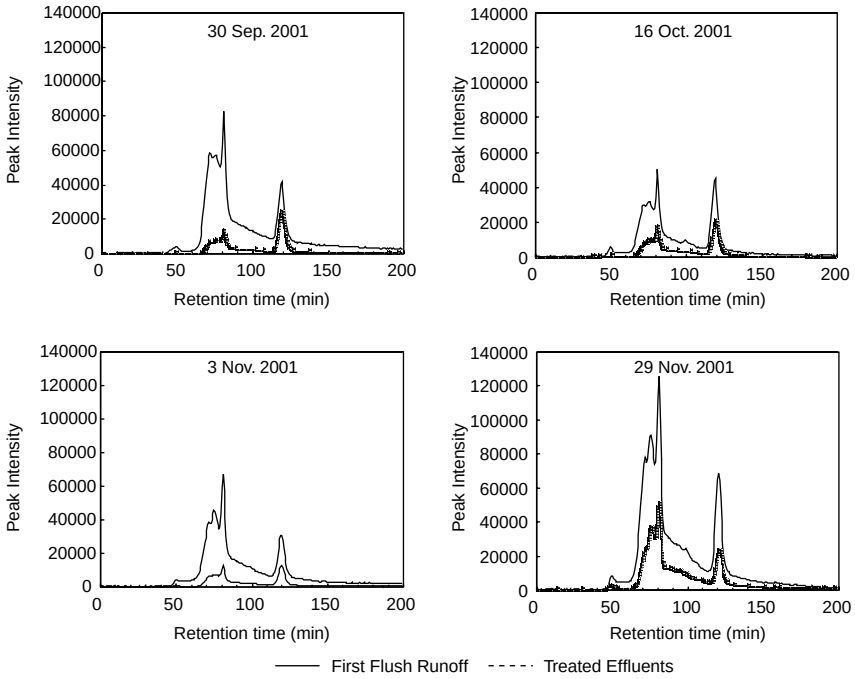

Figure 9 GPC-TC chromatograms of the experiments

If the peak intensity of the retention time of 70–80 minutes corresponds to the amount of the refractory dissolved organic substances, we can estimate the removal ratio of the refractory dissolved organic substances from the peak intensity using the TC analyzer. Therefore, we estimated that the refractory organic substances using this system reduce by approximately 70%; however, this is just the qualitative data. So we found that percolating through soil reduced the refractory dissolved organic substances and we successfully designed a system as a simple and easy experimental facility for urban runoff treatment.

Conclusions

Refractory dissolved organic substances are considered to be significant components causing an increase in the COD concentration in Lake Biwa. From our study, we found that refractory dissolved organic substances were high in road runoff and their concentrations were very high especially in the first stage of runoff. And taking advantage of the adsorption capability of organic matters by soil infiltration, we have suggested an effective countermeasure and instrument for reducing the supply of organic substances from road runoff to the lake. Detailed results obtained in our study were as follows.

- From GPC-TC analysis, easily decomposable and refractory dissolved organic substances were found to be contained in stormwater of road runoff. And refractory dissolved organic substances were considered to be less biodegradable.
- From field surveys of road runoff in rainfall events, COD concentration was found to be high especially in the first flush runoff, i.e. from the runoff start to 2.0 mm of integral flow.
- In experiments using the facility that selectively collects the first flush runoff and percolates it through soil, removal ratios of COD were found to be 77% for T-COD, 98% for P-COD and 54% for D-COD. And GPC-TC analysis confirmed that refractory dissolved organic substances were reduced by percolating the runoff through soil.

We consider that percolating the first flush runoff through soil is an effective and successful countermeasure for urban runoff treatment from the viewpoint of reducing COD components due to refractory dissolved organics. In future work toward its practical application, we consider it necessary to solve some maintenance issues, e.g. clogging of the soil surface, which is of critical importance for controlling its service life.

Acknowledgements

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