Characteristics of Leachate from Citrus Groves and their Changes in the Collecting Reservoirs in Matsuyama, Japan

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ABSTRACT
Matsuyama region, located in Shikoku Island, Japan faces the Seto Inland Sea on the west, where the annual rainfall is relatively less than in the other areas in Japan. In such favorable condition, the cultivation of citrus fruits is popular, and there are a large number of small reservoirs for irrigation purposes. The citrus groves are distributed in hilly areas surrounding the paddy fields and residential areas so there are higher chances for the nearby water environment to get affected by leachate from the groves. This paper investigates the water quality characteristics of the leachate from the groves, and studies the changes of the leachate quality near the collecting reservoirs. It was found that the grove soils are highly acidic and the leachate contains metals and nutrients in high concentration. On the other hand, the water quality of the leachate changed after it flowed into the reservoirs, and the concentrations became lower. It is understood that chemical and biological reactions help remove the contaminants in the reservoir, and from the standpoint of self-purification, reservoirs play an important role. This paper also discusses the kinetics of the self-purification and the quantitative estimation based on the experimental results.

Keywords: citrus grove, collecting reservoirs, leachate water quality

INTRODUCTION
Environmental problems caused by pollutants from non-point sources are one of the most significant issues in water environment. These pollutants are more difficult to control than those from point sources, because of their widely spread points of release and their runoff patterns such as low concentration and high amount of water. Social infrastructures like sewerage, water purification tanks (jokaso), and some wastewater treatment facilities have been constructed in Japan, whereas, pollutants from non-point sources have not been sufficiently controlled compared with those from the point sources. Therefore, the ratio of the amount of pollutants from a point source to the total amount of pollutants seems to be decreasing, and the relative impact of non-point source pollution to point source seems to be more and more significant. Pollutant runoff patterns depend on regional properties (Fujii et al., 2006), especially, agricultural areas which have become the major non-point sources of water pollutants in many parts of Japan.

For the management of these pollutants, understanding their exact behaviors is the first step to water environment management. Recently, with the development of computer tools such as geographic information system (GIS), more detailed analyses of the catchment areas or management of the water environment can be done easily and many researches have been carried out using GIS techniques. However, field surveys and detailed information that can be used for such system or techniques are necessary. Progress in both aspects is indispensable for an effective management of the water environment.
In this study, runoff characteristics of materials such as organics, nutrients and inorganic matters from a citrus grove were investigated, and their behaviors in the collecting reservoirs were considered with field survey and model experiment conducted in the laboratory.

Citrus fruits are intensively cultivated in several parts of Japan. Ehime Prefecture is one of those areas where citrus fruits are the main agricultural products. Matsuyama City, the prefectural capital with a population of about 500,000, meets the Seto Inland Sea on its west, which is one of the largest closed water areas in Japan and has required water purification for a long period. Aside from this, there are many small reservoirs in and around Matsuyama for multipurpose usage such as agriculture and urban life. There are citrus groves around the urban area of Matsuyama, which occupy more than 14% of the whole area. Therefore, it is considered that citrus groves are one of the largest non-point sources of pollutants from this region into the Seto Inland Sea. Water quality in the small reservoirs also seems to have been affected. However, field surveys about the runoff characteristics from citrus groves have not been abundant, and studies on the behavior of pollutants from the grove have not been sufficient either. Some parts of water from the grove do not directly run off to rivers but are retained for some period in the reservoirs located downstream (Nishimura et al., 2002). In this study, the behavior of the pollutants, especially nutrients, was surveyed in detail and material balances around reservoirs were considered.

**RESEARCH PROCEDURE**

**Location: Matsuyama region and periphery of the Seto Inland Sea**

The location of the research area and the distribution of the citrus groves in Matsuyama region are shown in Fig. 1. Matsuyama is situated in Shikoku Island in the southwestern part of Japan. The western side of the region faces the Seto Inland Sea, around which are...
some big and industrial cities like Osaka, Kobe, Hiroshima, and others. Therefore, it is considered that a large amount of pollutants runs into the sea from the urban as well as industrial areas. As the area around the Seto Inland Sea has a small amount of rainfall with a comparatively warm climate, the cultivation of citrus fruits is popular. The ratio of the citrus groves to the total land use is more than 10% in Ehime alone. Furthermore, it is reported that the pH of the grove soils is less than 4, and the soil contains nutrients such as nitrogen and phosphorus in high concentrations because of fertilization (Nishimura et al., 2010).

**Study area**
Field surveys were conducted in Taisanji area, as shown in Fig. 1, which is located in the northwestern part of Matsuyama region. The details of the area are given in Fig. 2. This area consists of small hills covered with citrus groves. The observations were made near the eastern side of a 110 m high hill where a kind of citrus called Iyokan is mainly cultivated. There are two small streams on the upper part of the hill and the streams flow together from 47 m above sea level. The water in the stream is the leachate from the grove and it flows into a collecting reservoir at the foot of the hill. The surface area of the reservoir is about 7300 m² and the average depth is about 2 m. The reservoir catchment area is estimated to be 0.23 km². Fertilization was conducted with mixed organic-inorganic fertilizer four times a year in March, June, September, and November. The total amount of the fertilizer used was 1.00 kg/m², which could provide 34 g-N, 24 g-P₂O₅ and 24 g-K₂O per unit area (m²). The grove soil was found to be strongly acidic. The chemical characteristics of the grove soil collected as a composite sample from several points in the study area are shown in Table 1.

![Fig. 2 - Location of sampling points](image)

(N33° 52’ 33”-30° 52’ 50”, E132° 43’ 34”-132° 44’ 07”), (WGS84)
Field observation

Field observations were conducted for about 19 months (from 26 May 2001 to 20 December 2002). The leachate from the grove, water in the streams, and water in the reservoir were collected periodically about once a week, and the onsite conditions such as weather, flow rate, and water temperatures of the leachate were observed. Samples were collected from 9 points. Four samples of leachate were collected from the upper part of the grove. The collection points Le.1, Le.2, Le.3, and Le.4 have elevations of 76m, 69m, 66m, and 60m, respectively. Stream water samples were collected at the middle parts of the grove from 4 points. Sampling points St.1 and St.2 are in the same stream, and sampling point St.3 is in the other stream. The two streams flow together to be one stream and the sampling point St.4 is situated in the joined stream, which is the only stream that flows into the reservoir. The reservoir water was also sampled from point Po. in the reservoir close to the outflow point. The collected samples were filtered immediately through glass microfiber filters of 1μm pore size (GF/B, Whatman) in the laboratory and water quality indexes such as concentration of nutrients, organic materials, cations, anions, metals, pH, and suspended solids (SS) were determined in conformity with standard methods (APHA/AWWA/WEF, 1998).

Experiments for the determination of kinetic constant of nitrogen conversion

Two lab-scale batch experiments were also carried out in order to examine the behavior of nitrogenous compounds in the reservoir. One was for nitrogen uptake by algae which had grown in the reservoir, and the other was for biological denitrification. Nitrogen uptake rate and denitrification rate were determined. The investigation of nitrogen uptake by algae followed a certain procedure. First, the reservoir water was collected and the algae in the water were separated and concentrated by centrifugation. Greater mass of the algae was Microcystis aeruginosa. Next, five kinds of culture solution based on the reservoir water were prepared. Four of them were prepared with different nitrate concentrations. The reservoir water was filtered (0.45 μm) and the filtrate was dispensed to vial containers, and KNO₃ was added. Nitrate concentrations were set as 0.5, 1.0, 2.0, and 5.0 mg-N/L for the four culture solutions. The other was an artificial culture solution based on MA medium and was used as a control (Watanabe M. F., 1996). All of them were sterilized with autoclave (120°C, 15 min.). The algae were then inoculated into the vial containers with the sterilized culture solution in order that the algal concentration was brought close to the original concentration. After that, they were set into a growth chamber under 12 hr-light (3000 lux)/12 hr-dark condition. Algal growth and the uptake of nitrogenous compounds were monitored by periodical measurement of the water quality such as chlorophyll $a$ (Chl.$a$), nitrate, nitrite, ammonia and dissolved nitrogen.

Table 1 - Chemical characteristics of the citrus grove soil

<table>
<thead>
<tr>
<th>pH*</th>
<th>exchangeable cations (water-soluble cations) [meq/100g soil]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H₂O)</td>
<td>Na⁺</td>
</tr>
<tr>
<td>4.25</td>
<td>2.08</td>
</tr>
<tr>
<td>(KCl)</td>
<td>(0.66)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CEC**</th>
<th>degree of saturation***</th>
<th>TP</th>
<th>water-soluble P</th>
</tr>
</thead>
<tbody>
<tr>
<td>[meq/100g]</td>
<td>[ - ]</td>
<td>[mg-P/100g]</td>
<td>[mg-P/100g]</td>
</tr>
<tr>
<td>9.05</td>
<td>1.41</td>
<td>228</td>
<td>4.28</td>
</tr>
</tbody>
</table>

* measured with H₂O or KCl (Mori and Shimada, 1975), ** Cation exchange capacity (Kuramoto et al., 1975), *** degree of saturation: [exchangeable cations]/[CEC]
Denitrification rate was also investigated. Biological denitrification is also one of the most important processes in conversion of nitrogenous compounds at reservoirs. Investigation for denitrification was carried out as follows. Reservoir water and sediments were first collected from the reservoir. The surface sediment within 10 cm from the bottom was sampled and the water close to the sediment was also collected for the experiment. Then a wide-mouth cylindrical bottle, with an inside diameter of 97 mm, was prepared as an incubator. The sediment of 60 g (wet weight) was added, and the filtered reservoir water or artificial culture solution was poured into the bottle. The reservoir water was filtered with 0.45 μm pore size membrane filter, and dilution water which is used for BOD measurement (APHA/WWA/WEF, 1998) was prepared as the artificial culture solution. After that, the water surface was covered and sealed by molten paraffin wax in order to prevent oxygen dissolution (Matsuyama and Ishizaki, 1982; Eisentraeger et al., 2001). Five cultivation cases were prepared; three of them used the reservoir water and the nitrate concentration was varied among them. The nitrate concentrations were set as 2.5, 5, and 10 mg-N/L. The other two cases used artificial culture. Potassium nitrate was added in order that the nitrate concentration became 5 mg-N/L in both cases, and glucose was also added only in one case. Both cases were setup for measuring the potential of denitrification activity. All of them were cultivated in the growth chamber under dark condition, and the temperature was maintained constant between 10°C and 30°C.

RESULTS AND DISCUSSION
Materials runoff characteristics and variation in the reservoir

Fig. 3 indicates time courses of nitrate concentrations of leachate, stream water, and reservoir water. The nitrate concentration in the leachate was found to be ranging from 4.5 to 85.2 mg-N/L, which is about 20 times higher than that in the environment with no effect of citrus groves. The main component of dissolved nitrogen was nitrate, and the ratio of nitrate to dissolved nitrogen was more than 80%. Likewise, the nitrate concentration in the stream water ranged from 5 to 43 mg-N/L, which was lower than that in the leachate. The concentration was found to be lower as the water flowed down. It ranged from 0 to 16 mg-N/L in the reservoir. Although the concentration became more than 10 mg-N/L, which is the water quality-based limitation, it was much lower than that of the leachate. It was seen that the concentration increased after heavy rainfall events, and decreased when the hydraulic retention time (HRT) of the reservoir became longer due to the depletion of influent quantity. The time course of the ratio of nitrate concentration to chloride ion (NO₃⁻/Cl⁻) in each water sample is shown in Fig. 3. Chloride ion concentration is relatively hard to be changed biologically as well as chemically. Therefore, if the value of NO₃⁻/Cl⁻ decreases, it can be considered that nitrate is removed from the water body. From the figure, it is understood that nitrate was certainly removed at the reservoir all throughout the year. The considerable processes for nitrate removal seemed to be photosynthesis by algae and biological denitrification at the bottom of the reservoir, since there were a lot of algae, especially during the summer season and the oxygen concentration at the bottom was 0-0.1 mg/L. General reaction formula of photosynthesis by algae and biological denitrification can be expressed as follows:
106 CO₂ + 122 H₂O + 16 NO₃⁻ + HPO₄²⁻ + 18 H⁺ → (CH₂O)₁₀₆(NH₃)₁₆(H₃PO₄) + 138 O₂ (1)

75 NO₂⁻ + 49 CH₃OH + 41 H₂CO₃ → 3 C₅H₇O₂N + 36 N₂ + 91 H₂O + 75 HCO₃⁻ (2)

120 NO₃⁻ + 53 CH₃OH → 3 C₅H₇O₂N + 59 H₂O + 117 NO₂⁻ + 35 H₂CO₃ + 3 HCO₃⁻ (3)

In each process, nitrate is removed biologically thus, alkalinity can increase. The observation results also showed that M-alkalinity increased from 0.8 meq/L at St.4 to 1.8 meq/L at the reservoir, and the pH ranged from 7.1 to 10.3 at the reservoir. The ratio of alkalinity increase to nitrate removal is in the considerable level suggested from equations (1) to (3) listed above. The behavior of phosphorus compounds was similar to that of nitrogenous compounds. Although they were also discharged in higher concentration compared with those observed in the surroundings, the concentration decreased at the reservoirs where it was in a range of 0.002 to 0.46 mg-P/L. The main component of phosphorus was phosphate, and the mechanisms of the phenomena were considered to be biological uptake and transition to the bottom due to the increase of pH. Other materials, such as heavy metals, were similar, and their concentration decreased at the reservoir. Water quality of the leachate from the citrus grove soil is summarized in Table 2. Their concentrations were found associated with the pH. The relationships between pH and heavy metals such as dissolved Al, Mn and Zn are shown in Fig. 4. Although the concentrations of dissolved Al and Mn in the leachate were high, pH increased through the stream and the concentrations of dissolved Al and Mn became lower. The pH value further increased and it reached basic conditions in the reservoir, and dissolved Al and Mn were removed more from the water. On the other hand, the removal of dissolved Zn was not so obvious. It is considered that soluble zinc hydroxide was formed under high pH condition. The removal mechanism of the metals seems to be chemical process such as hydroxide precipitation due to the increase of pH; however, the condition was led by biological reaction in the reservoir. Solubility curves of hydroxide precipitation are also illustrated in Fig. 4. Solubility curves of Al(OH)₃ almost coincides with Al concentration, whereas Mn(OH)₂ and Zn(OH)₂ do not coincide with Mn and Zn concentration. However, the tendency can be explained. Although the leachate can be a non-point source of pollutants to the surrounding environment, it is clearly understood that reservoirs that receive the leachate can remove pollutants through biological reactions.

**Biological conversion of nitrate and its kinetics**
According to the chemical reaction formula expressed above, nitrogen compounds can be consumed by algae during photosynthesis. In the lab-scale experiment, nitrate was

<table>
<thead>
<tr>
<th>pH</th>
<th>DOC</th>
<th>DN*</th>
<th>NO₃-N</th>
<th>NH₄-N</th>
<th>PO₄-P</th>
<th>DP*</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Pb</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>Si</th>
<th>Mn</th>
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<tbody>
<tr>
<td>Ave.</td>
<td>5.85</td>
<td>5.0</td>
<td>32.8</td>
<td>28.9</td>
<td>0.02</td>
<td>0.38</td>
<td>0.42</td>
<td>21.6</td>
<td>8.2</td>
<td>54</td>
<td>18.3</td>
<td>0.03</td>
<td>23.0</td>
<td>169</td>
<td>6.3</td>
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<td>Max.</td>
<td>8.47</td>
<td>13.2</td>
<td>85.3</td>
<td>85.2</td>
<td>0.25</td>
<td>2.23</td>
<td>2.97</td>
<td>40.1</td>
<td>21.8</td>
<td>122</td>
<td>44.2</td>
<td>0.33</td>
<td>43.0</td>
<td>387</td>
<td>26.5</td>
</tr>
<tr>
<td>Min.</td>
<td>4.15</td>
<td>1.8</td>
<td>6.5</td>
<td>4.5</td>
<td>N.D.</td>
<td>0.01</td>
<td>0.01</td>
<td>3.5</td>
<td>0.9</td>
<td>15</td>
<td>16.6</td>
<td>N.D.</td>
<td>9.0</td>
<td>50</td>
<td>N.D.</td>
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<tr>
<td>S.D</td>
<td>1.10</td>
<td>1.8</td>
<td>17.8</td>
<td>16.6</td>
<td>0.04</td>
<td>0.51</td>
<td>0.57</td>
<td>8.7</td>
<td>5.9</td>
<td>25</td>
<td>9.3</td>
<td>0.05</td>
<td>9.1</td>
<td>72</td>
<td>5.43</td>
</tr>
</tbody>
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Zn | Sr | Al | Ba | B | Fe | As | Mo | Cr | Se | Ni | Co | Cu | Sb | V | Cd |
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<tbody>
<tr>
<td>Ave.</td>
<td>0.36</td>
<td>0.32</td>
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<td>0.11</td>
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<td>0.03</td>
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<td>0.01</td>
<td>0.01</td>
<td>0.003</td>
<td>0.001</td>
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<td>Max.</td>
<td>8.74</td>
<td>0.69</td>
<td>1.04</td>
<td>1.00</td>
<td>1.12</td>
<td>0.69</td>
<td>0.12</td>
<td>0.16</td>
<td>0.26</td>
<td>0.19</td>
<td>0.11</td>
<td>0.02</td>
<td>0.05</td>
<td>0.06</td>
<td>0.023</td>
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<tr>
<td>Min.</td>
<td>0.02</td>
<td>0.08</td>
<td>N.D.</td>
<td>0.04</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
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<tr>
<td>S.D</td>
<td>0.97</td>
<td>0.15</td>
<td>0.31</td>
<td>0.11</td>
<td>0.12</td>
<td>0.08</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.004</td>
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</table>

Notes: DN means dissolved nitrogen and DP means dissolved phosphorus.
removed from the culture solution as the algae from the reservoir grew up. The ratio of the nitrate consumption to the algal growth was in the range of 48-70 μg-N/μg-Chl.a. There was no clear tendency of temperature dependency, however. The nitrogen removal rate was up to about 10 μg-N/μg-Chl.a/day. The relationship between nitrate concentration and the removal rate is shown in Fig. 5. The removal rate becomes larger with the increase in nitrate concentration. It is reported that nitrate concentration had effect on specific growth rate and that the growth rate was not affected if nitrate concentration was more than 1 mg-N/L (Yagi et al., 1981), and N/Chl.a ratio was 18.1 or 9.1 μg-N/μg-Chl.a (Takamura et al., 1981; Yagi et al., 1981). In this study, nitrate removal rate was found to increase with the increase in its concentration if the concentration was less than 2 mg-N/L, and the ratio of the nitrate consumption to the algal growth was found higher than the one reported earlier. It is considered that some other microorganisms such as bacteria also played some role along with the algae, because it was observed that SS were also increased through the cultivation and the ratio of the increased amount of SS to the increased amount of Chl.a was higher than that of the algae. Increased amount of SS were higher in the cases of high nitrate concentration.

Fig. 3 - Time course of Chl.a, nitrate and its ratio to chloride ion

Fig. 4 - Relationship between pH and metals(Al, Mn, and Zn)
S.C : solubility curves of hydroxides precipitation
On the other hand, denitrification rate, which can be defined as a linear function of nitrate concentration (i.e., the denitrification is first-order reaction of nitrate), was strongly affected by the nitrate concentration. Relationship between nitrate concentration and denitrification rate is shown in Fig. 6. The experimental formula for denitrification is as follows:

$$ R_D = k_n \cdot C_n $$  \hspace{1cm} (4)

where, $R_D$ is the denitrification rate (mg-N/m$^2$/day), $k_n$ is the rate coefficient (L/m$^2$/day) and $C_n$ is the nitrate concentration (mg-N/L).

The coefficient, $k_n$ was calculated as 20 - 50 (ave.23) (L/m$^2$/day) at 10 - 20°C, when nitrate concentration was less than 7 mg-N/L. Organic carbon for denitrification was supplied from the sediment. The denitrification rate was raised to be about double when glucose was added as an electron donor. Although organics from the sediment were not as well available as glucose, it can be considered that almost half or more of the potential of the denitrifying activity was exploited. The dissolution rate of organic matter from the sediment was sufficient, and limitation of denitrification caused by depletion of electron donor did not happen during the experiment.

The nitrogen balance around the reservoir was roughly estimated using kinetics obtained from the experiments. The assumed transformation paths in the reservoir were denitrification and nitrogen removal associated with algal activity such as uptake. It was also assumed that inflow was mainly from stream water, and nitrate and particle nitrogen such as algae itself were major components in the effluent. Time course of Chl.a concentration is shown in Fig. 3. The maximum Chl.a concentration was 8700 μg/L and the average value was 315 μg/L. During the 573 days of observation, 7800 kg-N of nitrogen flowed in, 10% of nitrogen was denitrified biologically, and 40% of it was removed by algal activity. Almost 50% of nitrogen out-flowed from the reservoir, 35% was nitrate and the remaining seemed to be particle component. They flowed out mainly during the rainy days.
CONCLUSIONS
In this study, runoff characteristics of the materials from citrus grove were investigated and their behaviors in the collecting reservoirs were discussed. The main results obtained from the investigation are as follows:

1) Nitrogen concentration in grove soil leachate ranged from 4.5 to 82.5 mg-N/L, and the main component was nitrate, whereas phosphorus concentration was up to 0.46 mg-P/L, and the main component was phosphate. The concentration of nutrients was much higher than that in the surrounding environment.

2) The pH of the leachate was low, and many kinds of metals were also found dissolved in it. However, the pH increased as the leachate flowed down through the stream into the reservoir. Biological activity seemed to have raised the pH, and some kind of metals might have been removed due to the pH increase.

3) Nitrate was removed in the reservoir by denitrification and the biological activities associated with photosynthesis. The removal efficiency was estimated to be 50%, which was expected to rise further during the absence of rainy days.

Finally, the leachate from the citrus grove can be a non-point source of pollutants to the surrounding environment, but it is experimentally shown that reservoirs which receive the leachate can remove pollutants through biological reactions.

REFERENCES


