Environmental Pollution 243 (2018) 308–317

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Major and minor elemental compositions of streambed biofilms and its implications of riverine biogeochemical cycles☆

Naoki Mori [a, 1], Kenichiro Sugitani [a, *], Mariko Yamamoto [a], Rie Tomioka [b], Miyako Sato [c], Naomi Harada [c]

[a] Graduate School of Environmental Studies, Nagoya University, Nagoya, 464-8601, Japan
[b] Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya, 464-8601, Japan
[c] Japan Agency for Marine-Earth Science and Technology, Yokosuka, 237-0061, Japan

ARTICLE INFO

Article history:
Received 17 April 2018
Received in revised form
28 July 2018
Accepted 2 August 2018
Available online 7 August 2018

Keywords:
Streambed biofilm
Chemical compositions
Dam reservoir
Heavy metals

ABSTRACT

Chemical compositions of streambed biofilms from a major river of central Japan (the Kushida River) were obtained, with data of associated sediments (fine-grained fractions < 63 μm) and dissolved components of waters, in order to provide preliminary information about biogeochemical significance of streambed biofilms. During the sampling period (July 31st to August 3rd, 2013), dissolved components of the river waters were influenced by the dam reservoir. Concentrations of NO_3^-, silica (as Si), SO_4^{2-}, PO_4^{3-} and Ca^{2+} decreased across the dam, whereas Fe and Mn increased across the dam, and then decreased downstream rapidly. Streambed biofilms contain significant amount of non-nutrient elements such as Al (up to 21% as Al_2O_3 on water and others-free basis), indicating that they are contaminated as siliciclatic (silt and clay) materials. Siliciclastic materials in the biofilms are basically compositionally similar to fine-grained (<63 μm) fractions of streambed sediments. However, some elements such as Ca, P, Mn, and Zn are markedly enriched in the biofilms. Particularly, Mn concentrations in the biofilm samples collected just below the dam reservoir are very high (~4.0 wt %), probably due to accumulation from the discharged water. Concentrations of trace elements such as P, Cr, Cu, Zn and V appear to be controlled by amounts of Fe-oxides and/or Mn-oxides in biofilms. Numbers of factors are involved in controlling chemical compositions of streambed biofilms, including amount of contaminated siliciclastics, authigenic mineral formation, adsorption of dissolved materials and microbial metabolisms. As demonstrated by this study, systematic analyses including major elements and comparison with associated sediments and waters could reveal biogeochemistry of this complex system.

1. Introduction

Streambed biofilms composed mainly of microbes and extracellular polymeric substances (EPS) are quite complex systems. They have been studied extensively in the context of microbial community compositions, and primary production and nutrient cycles of river ecosystem, and metal accumulation mechanisms (e.g, Battin et al., 2003; Besemer et al., 2009; Dranguet et al., 2017; Drahota et al., 2014; Konhauser et al., 1994a,b; Tani et al., 2003). Biofilms can be regarded to represent consortia of primary producers in river ecosystem, and are fed directly or indirectly as POM (Particulate Organic Matter) by aquatic organisms such as grazers and collectors. Thus these primary consumers and those of higher trophic levels could be affected by chemistry of biofilms (e.g., Ancion et al., 2013; Farag et al., 2007; Rhea et al., 2006). For example, Farag et al. (2007) demonstrated that metal concentrations in biofilms and in aquatic invertebrates are closely related with each other. Also, Ancion et al. (2013) reported that three trace metals (Zn, Cu & Pb) in biofilms explained the community variations in bacteria and ciliate protozoa more than those in sediments. Significance of inorganic geochemistry of streambed biofilms has been well demonstrated by these studies and others (e.g., Haack and Warren, 2003; Kamjunke et al., 2015). To our knowledge, however, these and other previous geochemical studies of streambed biofilms did not provide dataset of major elements as Si, Al, Ti, Fe, Mn, Mg, Ca, Na, K and P, despite concentrations of these

☆ This paper has been recommended for acceptance by Joerg Rinklebe.

* Corresponding author.
E-mail address: sugi@info.human.nagoya-u.ac.jp (K. Sugitani).
[1] Present address: JCB Co. Ltd., Nagoya 460-0003, Japan.

https://doi.org/10.1016/j.envpol.2018.08.007
0269-7491/

elements provide basic information about what components contribute to biofilm chemical compositions and are expected to give insights into dynamics of trace metals in biofilms. Thus, the purposes of this study are to present the first comprehensive dataset of major and minor elemental compositions of streambed biofilms, providing basis on how biofilms contribute to biogeochemical cycles in the stream ecosystem.

2. Materials and methods

2.1. Sampling area

The Kushida River originates from the Mount Takami (alt. 1, 249 m) at the border between Mie Prefecture and Nara Prefecture in central Japan. It flows 87 km into the Ise Bay and its basin area is 436 km^2 (Fig. 1). The basement of the northern part is composed mainly of granitic rocks, whereas that of the southern part consists of schists (Geological Survey of Japan, 2014). Population at the upper and the middle reaches is 15, 000 persons and that at the lower reaches is 16, 000 persons. The basin of the Kushida River is occupied largely with forests, paddy and tea fields, and residential lands. Industries are also present but of small scale. The Kushia River water during the sampling season can be assumed to be pristine and its trophic level is very low, as demonstrated by low BOD concentration (<1 mg/l) (Chubu Regional Bureau, 2013a). The Kushida River has many tributaries, most of which, except for the Hachisu River and the Sana River, are very small. The Hachisu River is located at the uppermost reaches and has a large dam (the Hachisu Dam) with height of 78 m, effective water depth of 41 m, and effective storage capacity of 29,400,000 m^3 (Chubu Regional Bureau, 2014). The residence time of water in the dam reservoir is calculated to be 78 days, based on an average inflow rate (4.30 m^3/S) in 2009 and the effective storage capacity.

2.2. Sampling and sample treatment

The samplings were performed from July 31st to August 3rd, 2013. We collected 31 water samples including 6 samples from the Hachisu River and 5 reference samples from drainages and small tributary, which were not used for this study (Fig. 1). Although we intended to collect biofilms and sediments at the same localities for the water samples, actual collected number of biofilms are 26, among which only 17 samples were enough in amount for analyses of major and minor elements. Sediment samples used for chemical analyses of fine fractions (<63 μm) were collected mainly from dips of exposed boulders in stream and shores of the river. We collected and analyzed 21 sediment samples, among which 17 samples corresponding to biofilm samples were used in this study.

Water samples were filtered on site (<0.45 μm) and stored pre-cleaned polyethylene bottles (100 ml). For samples subjected to heavy metal analyses, polyethylene bottles were pre-washed with HNO_3 and 0.5 ml HNO_3 were added to the samples immediately back to the laboratory. Streambed biofilms were removed from gravels using a plastic brush and suspended in a plastic bowl to

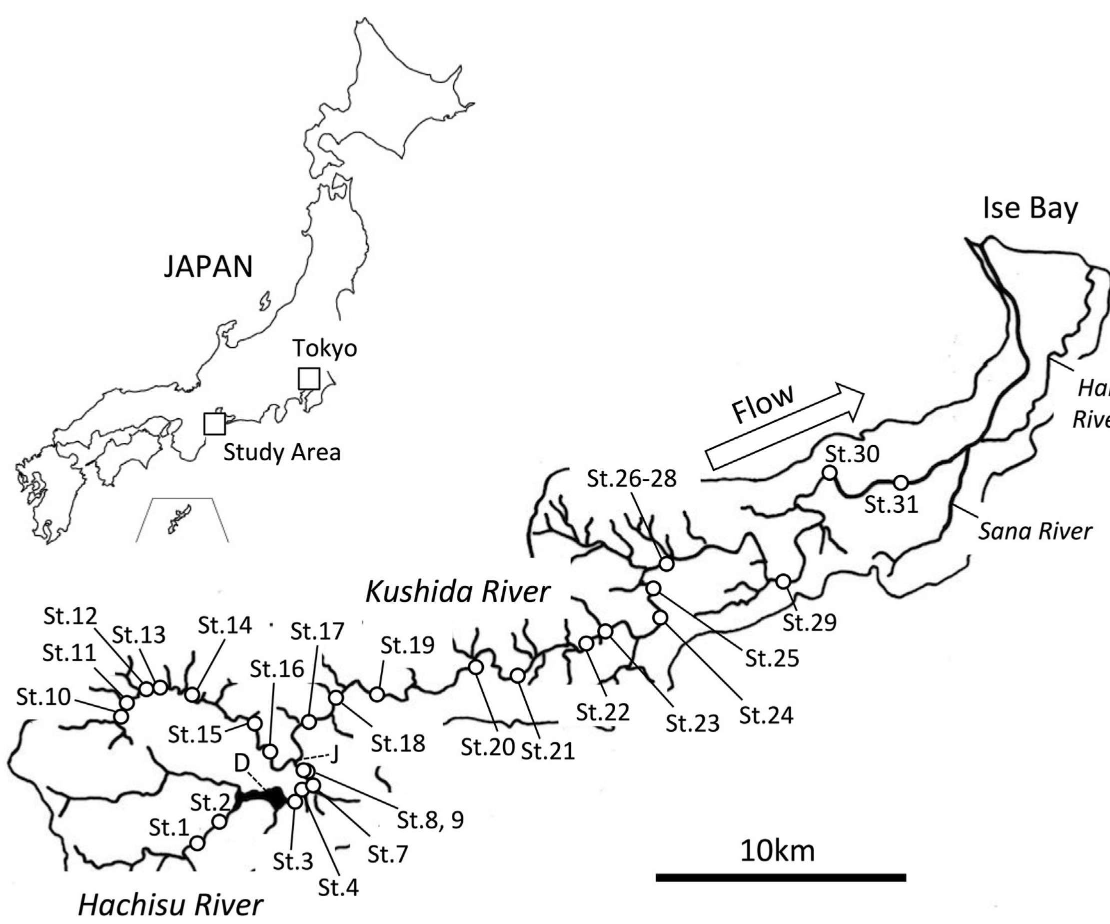

Fig. 1. Sampling Localities. D and J show the Hachisu dam and the junction, respectively. Stations 5 & 6 are not shown, because these correspond to sampling sites at the small tributary of Hachisu River and are not used in this work.