Summary of Doctoral Thesis

Enrollment year: 2013/03
UGAS Specialty: Bioenvironment
Name Susan PRAISE

Title	A study on manganese, iron and dissolved organic matter in mountainous streams with sabo dams

Introduction and purpose

Due to the mountainous nature, in Japan, Sabo dams have been used for many years to prevent the impact of disasters and their use has been expanding worldwide (Chanson, 2004). Rivers and streams are dynamic systems involving a variety of elements, some of which interact with each other in a continuous water flow movement linking terrestrial ecosystems to oceans. Inland water systems receive substantial amounts of organic matter accompanied by high metal loading from soil erosion and rock weathering in mountainous areas. Organic matter consists of both dissolved and particulate forms which are easily separated using filtration. Dissolved organic matter (DOM) has various functional groups which interact strongly with trace metals creating avenues for immobilization and transport (ElBishlawi and Jaffe, 2015). Trace metals exist in the environment as a function of surface runoff from terrestrial areas, groundwater mixing, sediment dissolution, atmospheric deposition, redox condition and anthropogenic activities (Mohuiddin et al., 2012). Natural waters contain a variety of trace metals which tend to exist in more than one oxidation state and have affinities for both soft and hard ligands (Warren and Haack, 2001). DOM complexation with trace metals subsequently determines the fate of metals and carbon along the stream continuum. DOM chemistry and composition are highly variable and depend on various factors such as source, temperature, pH, ionic strength, surface chemistry and system microbiology (Leenheer and croue, 2003; Ren et al., 2015).

Damming of rivers is important in many ways such as electricity generation, water supply for agriculture, industrial and domestic uses and mostly flood control. However, dams alter river morphology and spatial connectivity, interfere with hydrological regime and residence time (Frield and Wuest, 2002) in addition to creating areas with either higher reaction rates than the surrounding or short periods with relatively higher reactions than longer times (McClain et al., 2003). Small dams which are approximately 80,000 worldwide have received very little scientific attention yet their impacts may be far greater than big dams (March et al., 2003). Dams create reservoirs which enhance in-situ primary production, evokes particle settling, decreases turbidity and affect light transmissivity (Friedl and Wuest, 2002). Such environmental changes affect not only the biogeochemical cycling of trace metals but also DOM properties. Two metals, iron (Fe) and manganese (Mn), have a significant environmental relevance and influence other metals through co-precipitation. However, these metals are easily affected by changes in environmental condition resulting from damming. This study was conducted with the aim of elucidating the impact of sabo dams on DOM and the behavior of trace metals in mountainous streams under three specific objectives

1. To investigate how sabo dams affect trace metals (manganese and iron) along the stream continuum
2. To find out how DOM quantity and character is affected by sabo dams
3. To find out how changes in DOM quality and quantity are related to manganese (Mn) and iron (Fe) behavior in streams with sabo dams

Materials and methods

This study was carried out in Yamagata prefecture, Japan. Surface water samples were collected from five mountainous streams namely; Mizunashigawa (MIZ), Higashiiwamotogawa (HIG), Kanosawagawa (KSW), Imogawa (IMO) and Maenokawasawa (MNK) from June to November 2015. The water samples were collected from four stations in each stream located in the upstream, in the dam reservoir and dam outflow, at the confluence to the higher order of stream. Among the sampling stations, the confluence stations alone had anthropogenic influences from agricultural, commercial and domestic activities in the surrounding environment. Water samples were filtered in the field using 0.45μm filters, both unfiltered and filtrate samples were analyzed in the laboratory for total and dissolved elements respectively. The water samples were analyzed for both trace metals (Fe, Mn, Al, Cu, Zn, Pb, Ni, Cr, and Cd) and organic matter.

Metal analysis was done using ICP-mass spectrometry after acid digestion while DOM properties were analyzed with a combination of ultraviolet-visible and fluorescence spectroscopy.

DOM properties were described using ultraviolet absorbance indicators; specific ultraviolet absorbance ($SUVA_{245}$), spectral ratio (S_R), molecular weight indicator (E2:E3), along with components identified by excitation-emission fluorescence with parallel factor analysis (PARAFAC).

Analysis of variance (ANOVA) and Tukey tests were used to compare metal concentrations between sites and stations respectively. In addition, Pearson correlation coefficients, hierarchical cluster analysis, paired t-test and principal components analysis (PCA) were used.

Results

From the results, total Fe concentration varied between five streams ($F(4,87)=3.01$, $p=0.022$), while total Mn concentration did not ($F(4,87)=2.00$, $p=0.101$). A statistical analysis of all samples combined demonstrated significantly high concentrations of Mn and Fe at the stations in the dam vicinity, in other words, at the inside, and below the sabo dams. The Mn concentration was also found to decrease between dams following the exponential equation: $[MnTot]=[MnTot]_0\exp(-kx)$, where k is conditional stability constant for the redox reaction and x is the distance from the dam. Out of the nine metals analyzed, Fe and Mn showed a similar pattern with significantly higher concentrations around the dam whereas Cd concentrations were very low at all the stations throughout the sampling period.

UV-visible properties showed an increase in DOM molecular weight composition and aromaticity around the sabo dams. Three components of DOM, namely fulvic acid-like (C1), humic acid-like (C2) and tryptophan like (C3), were successfully identified by PARAFAC analysis (Fig.1).

These components together with fluorescence indices gave further insights into DOM dynamics. Contrary to $SUVA_{245}$, S_R, and E2:E3 values, PARAFAC components did not exhibit significant changes around the dam but rather increased towards the downstream. As expected, the fulvic acid-like component was more indices emphasized the dominance of terrestrial-derived DOM from vascular plants, soil pore water, and abundant, however, the observed ratio for C1:C2 was less than our expectation (>4) based on the previous reports by other researchers. Fluorescence index values (≥1.4) implied that DOM dominant at all stations were from terrestrial origins. Furthermore, values of biological and humification sediment source. DOM concentration showed significantly higher value at the confluence, indicating that DOM concentration along the streams was largely influenced by anthropogenic activities, while its aromaticity and molecular composition was mostly transformed by sabo dams.

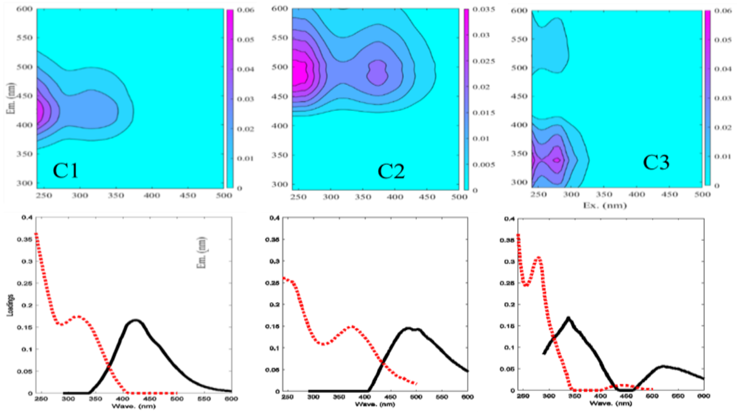

Fig 1. Three components identified from PARAFAC analysis

Various statistical analyses on the association between Fe, Mn and DOM composition at different sections of the stream manifested strong relationships among these elements. For example, we found a significant correlation ($r=0.60$, $p<0.05$) between EEM component C1 and dissolved Mn, while dissolved Fe was not associated with this EEM component. SUVA245 was significantly correlated with both dissolved Mn ($r=0.66$, $p\leq0.001$) and Fe ($r=0.79$, $p=0.001$). Principal components analysis demonstrated that the 1st and 2nd components composed of dissolved Mn and Fe, together with DOM concentration and properties, and accounted for 42.5% variation in all samples. Also, a positive linear relation was found between fulvic acid-like fractions and dissolved metals at the two stations inside and below the sabo dams, whereas, the correlation was negative at the upstream and downstream stations. Based on hierarchical cluster analysis using dissolved metals, DOM concentration, and properties, the stations inside and below the dam at Mizunashigawa river were classified into a different cluster from other stations at both Mizunashigawa and Higashiiwamotogawa rivers. These two major clusters did not only emphasize the high impact of sabo dams but also further disclosed the site-specific factors such as dam size, capacity, and nature of retained materials. One of the unique characteristics of the sabo dam which may have contributed to the association between metals and DOM along Mizunashigawa river is that the reservoir was nearly filled with sediments has been transformed to a wetland, as well as that reservoir water was discharged from outlet vents in the dam wall. The impact of sabo dams on Mn concentration was more obvious at Mizunashigawa and Kanosawagawa. Moreover, both Fe and Mn concentrations were significantly high at stations around the sabo dams at Mizunashigawa, revealing that sabo dams may intensely affect metal transformations along the continuum through alteration of environmental conditions enhancing dissolution of stable hydroxides and oxides.

Conclusion and consideration

This study highlights the impacts of sabo dams on Mn, Fe and DOM behavior. It was revealed that sabo dams surely affect environmental dynamics of both trace metals and DOM by modifying DOM characteristics which enhance solubilization of metals, resulting in the increase in their concentrations. In sabo dams without overflows and large reservoirs, the impacts may be more evident and stronger than anthropogenic inputs as observed at Mizunashigawa, however, this relies upon watershed characteristics such as vegetation and sediment delivery. Changes in physicochemical characteristics of the watershed have a potential to alter the stream environment and ecosystem as a consequence the fate many elements highly influenced by DOM especially in the presence of Mn and Fe.

DOM and trace metals play an important role in the environment, therefore, further studies should be conducted to elaborate on this important topic. With the expansion of sabo dam usage, an in-depth study on the fate of both Mn and DOM together with other elements in mountainous streams with a high density of sabo dams is necessary. This will provide more details on how Mn DOM and sabo dams affect the other elements, especial other metals which may have harmful effects on ecosystems. Furthermore, it is important to link DOM and metals to specific environmental characteristics and examine sediment profiles from reservoirs to highlight the important processes responsible for the observed pattern along the continuum. In addition, analytical techniques that can quantify both temporal and spatial changes in watershed characteristics, and other factors such as hydrological events, light penetration and residence time within the dam reservoir, and those that can examine DOM compounds in detail such as high-performance liquid chromatography (HPLC) should be incorporated any further studies.

References.

Chanson, H., 2004. Sabo check dams-mountain protective systems in Japan. International Journal of River Basin Management 2:301–307.

ElBishlawi H, Jaffe PR (2015) Characterization of dissolved organic matter from a restored urban marsh and its role in the mobilization of trace metals Chemosphere 127:144-151 doi:10.1016/j.chemosphere.2014.12.080

Friedl G, Wüest A (2002) Disrupting Biogeochemical Cycles—Consequences of Damming. Aquatic Sciences 64:55-65. doi:10.1007/s00027-002-8054-0

Leenher JA, Croué J-P (2003) Organic matter characterization. Aquatic organic matter; Understanding the unknown structures is key to better treatment of drinking water. Environmental Science & Technology 37 (1), 18A–26A: doi: 10.1021/es032333c

March JG, Benstead JP, Pringle CM, Scatena FN (2003) Damming Tropical Island Streams: Problems, Solutions, and Alternatives BioScience 53

McClain ME et al. (2003) Biogeochemical Hot Spots and Hot Moments at the Interface of Terrestrial and Aquatic Ecosystems Ecosystems 6:301-312 doi:10.1007/s10021-003-0161-9

Mohiuddin KM, Otomo K, Ogawa Y, Shikazono N (2012) Seasonal and spatial distribution of trace elements in the water and sediments of the Tsurumi river in Japan Environmental monitoring and assessment 184:265-279 doi:10.1007/s10661-011-1966-1

Warren LA, Haack EA (2001) Biogeochemical controls on metal behavior in freshwater environments Earth-Science Reviews 54:261-320 doi:10.1016/s0012-8252(01)00032-0