A Raman imaging study of the ecocorona surrounding microplastics in aquatic environments

Tatsuyuki Yamamoto[1,2], Edward Gou Nagato[1], Hidetoshi Sato[3], and Hemanth Noothalapati[2,4]
[1]*Faculty of Life and Environmental Sciences, Shimane University*
[2]*Raman Project Center of Medical and Biological Apllications*
[3]*School of Science and Technology, Kwansei Gakuin University*
[4]*Research Administration Office, Shimane University*

The distribution of microplastics (MPs) in the ocean is a global environmental issue. One recent report indicated that the averaged concentration of MPs at five points from Tasmania Island to the Southern Ocean near Antarctica, was about a hundred thousand MP particles/km^2 [1]. There are numerous sources that span from the fragmentation of larger plastics flowing from terrestrial rivers to the direct deposition from fisheries activities. However, MPs have also recently been detected in atmospheric samples in high mountains and characterized using Raman spectroscopy [2]. Atmospheric deposition then represents another vector for MP contamination in aquatic environments. These plastic surfaces are known to be the substrates for bacteria colonization, forming an "ecocorona," which can alter the environmental fate and behavior of these contaminants. In addition, there is also the deposition of atmospheric $PM_{2.5,}$ which carry polycyclic aromatic hydrocarbons (PAHs) [3]. It is not clear how environmental contaminants may interact with the bacteria colonies around MPs and these may be sites for the creation of even more harmful PAH congeners.

Figure 1. An example bacterial assemblage prepared in a Winogradsky column using local sediment and water.

In this context, we have planned a series of experiments on examining the bacterial colony (ecocorona) formation around MPs in aquatic systems. In this study, we will examine the growth of ecocoronas, using microbes collected from local environments, cultured in Winogradsky columns (Figure 1) in the presence of polystyrene (8 μm) MPs. Ecocorona growth will be monitored using dynamic light scattering and Raman spectra will help characterize the ecocorona as well as the metabolites that surround the growing polystyrene particle. We will utilize a non-negative restricted multivariate curve resolution technique followed by singular value decomposition, to analyze the two-dimensional Raman spectra to acquire Raman images [4]. In the raw Raman spectra are overlapping varieties of pure Raman spectral components with different intensities. The intensity and spectral features for each pure Raman spectrum are calculated by the procedure mentioned above. All obtained pure Raman spectral components are physically meaningful because physically meaningless components with negative band intensities are excluded by the non-negative restriction condition. Thus, obtained intensity distributions for calculated pure Raman spectral components give Raman images, which show the molecular distribution of chemical compounds in the MP ecocorona. We are expecting to obtain time course images of the molecular distribution of chemical compounds in the ecocorona. Through these experiments, we believe we will acquire clues to the structural changes of MPs and the potential transformation of PAHs in aquatic environments. Our aim at this meeting is to report on the growth of ecocorona and the Raman images observed.

References

1. Isobe A., et al., Microplastics in the Southern Ocean, *Marine Pollution Bulletin*, **114**, 623-626, 2017
2. Allen S. et al., Atmospheric transport and deposition of microplastics in a remote mountain catchment, *Nature Geoscience*, **12**, 339-347,2019
3. Hayakawa K. et al., Polycyclic aromatic hydrocarbons as a marker of $PM_{2.5}$ in East Asia, *Jpn. J. Clin. Ecol.*, **23**, 93-101, 2014
4. Noothalapati, H. et al., Label-free Chemical Imaging of Fungal Spore Walls by Raman Microscopy and Multivariate Curve Resolution Analysis, *Sci. Reports*, **6**, 27789, 2016.