



## An autonomous drifting buoy system for long term pCO<sub>2</sub> observation

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Many studies have been carried out around the world to understand what happens to carbon dioxide (CO<sub>2</sub>) once it is emitted into the atmosphere, and how it relates to long-term climate change. However, the sea surface pCO<sub>2</sub> observations on volunteer observation ships and research vessels concentrated in the North Atlantic and North Pacific. To assess the spatial and temporal variations of surface pCO<sub>2</sub> in the global ocean, new automated pCO<sub>2</sub> sensor which can be used in platform systems such as buoys or moorings is strongly desired. We have been developing the small drifting buoy system (diameter 250-340 mm, length 470 mm, weight 15 kg) for pCO<sub>2</sub> measurement, with the support of the Japan EOS Promotion Program (JEPP), the Ministry of Education, Culture, Sports, Science and Technology (MEXT). The objective is to provide simplified, automated measurements of pCO<sub>2</sub> over all the world's oceans, an essential factor in understanding how the ocean responds to climate change.

The measurement principle for the pCO<sub>2</sub> sensor is based on spectrophotometry (e.g. Lefèvre et al., 1993; Degrandpre et al., 1995). The CO<sub>2</sub> in the surrounding seawater equilibrates with the indicator solution across the gas permeable membranes. The equilibration process causes a change of pH in the indicator solution, which results in the change of optical absorbance. The pCO<sub>2</sub> is calculated from the optical absorbance of the pH indicator solution equilibrated with CO<sub>2</sub> in seawater through a gas permeable membrane. In our analytical system, we used an amorphous fluoropolymer tubing form of AF-2400 by DuPontTM for the gas permeable membrane due to its high gas permeability coefficients. The measurement system of the sensor consisted mainly of a LED light source, optical fibers, a CCD detector, and a downsized PC. The measured data were transmitted to the laboratory by satellite communication (Argos system). In the laboratory experiment, we obtained a high response time (less than 2 minutes) and a precision within 3  $\mu$ atm.

One of the challenges we faced was developing an anti-biofouling paint for the buoy and pCO<sub>2</sub> sensor. When the buoy system is utilized for long-term observations, the instruments are susceptible to biofouling, in the form of microbial and algal films. Minimizing toxicity is important for the buoy system. In order to reduce the effects of biofouling on the sensors, we tried the antifouling tests with some paints in our port side (Aomori, Japan) for 18.5 months. We avoided using metal (Cu, Zn) type paint despite good results because our buoy is made of aluminum. Following tests, the silicon type paint was adapted as an anti-biofouling paint for drifting buoy.

To test the long-term durability and effect of anti-biofouling, the buoy systems were moored with TRITON buoy in the western tropical Pacific Ocean (2N, 156E) and with K-TRITON buoy in the western North Pacific Ocean (38N, 146.5E). Our first deployment of drifting buoy system was made in the east Labrador Sea in May 2008, with the support of the Bedford Institute of Oceanography. The buoy system is measuring sea-surface pCO<sub>2</sub> four times a day (also collecting temperature and salinity data) and every six days intervals, because of limited battery capacity. We succeeded in obtaining the data for six months.

We will need to perform some laboratory experiments and an in situ long-term test for the buoy system. As a result of our tests, some components will be modified. We hope to produce the improved buoy system on a wide-scale. In order to have a network of pCO<sub>2</sub> observation all over the world's ocean, the buoy must be produced at a reasonable cost. The goal of keeping costs within limits is one of the important aspects in the development. We aim for that one buoy cost \$ 15,000 or less when large numbers of buoys are produced.