Alkalinity measurement quality improves for PICES nations

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As one of its terms of reference, the PICES Working Group 13 on CO_2 in the North Pacific is working to improve measurement quality. To achieve this, the Working Group planned to carry out a series of between laboratory comparisons of measurement techniques for the parameters: total dissolved inorganic carbon, total alkalinity, and the $^{13}C/^{12}C$ ratio of the inorganic carbon in seawater. The first of these PICES-sponsored exercises took place in early 1999, and was organized collaboratively by the National Institute for Environmental Studies (NIES, Tsukuba, Japan) and the National Institute for Resources and Environment (NIRE, Tsukuba, Japan) and the Scripps Institution of Oceanography (SIO, La Jolla, U.S.A.). Samples were distributed to 13 participating laboratories from 5 countries, and this was followed up by a technical workshop in Tsukuba in April 1999 (for details see PICES Press Vol 7, No. 2).

A principal focus of the workshop was a detailed discussion of the results obtained for the inter-laboratory comparison. The measurements of total dissolved inorganic carbon were very encouraging. Once the data had been adjusted using the measurement on CRM (Certified Reference Material) Batch 45 so as to allow for calibration problems, all the results from the various laboratories involved were consistent with each other and within ±5 µmol/kg of the certified value. However, for the measurement of alkalinity, though a calibration adjustment improved the degree of agreement, there were still significant discrepancies of up to ±25 µmol/kg from the certified value. It was thus agreed that the next inter-comparison study would focus on the measurement of total alkalinity in seawater.

Discussion at the second PICES CO_2 Technical Workshop held October 20, 2000, at the EPOCHAL International Congress Center, Tsukuba, Japan.

Dr. Andrew G. Dickson (indicated by arrow) is an Associate Professor-in-Residence at the Scripps Institution of Oceanography of the University of California, San Diego, and a member of PICES Working Group 13 on CO_2 in the North Pacific. His research interests include the study of the oceanic carbon dioxide system as well as other aspects of ocean biogeochemistry. He plays a major role in organizing inter-calibration and quality control for CO_2 measurements in seawater.

This PICES sponsored study – again a collaborative effort between SIO and NIES/NIRE – was carried out this year, and followed up with a technical workshop held October 20, 2000, in Tuskuba, Japan. Again, four samples were distributed for analysis by the participating laboratories (1 from Canada, 7 from Japan, 1 from Korea, 1 from Russia, and 3 from the U.S.A.). Twenty four scientists, members of the participating laboratories together with some observers, attended this workshop. Similar results were obtained for total dissolved inorganic carbon as in 1999 (again after adjusting for small calibration problems). For alkalinity, the results were significantly better than they had been in 1999. With the exception of two participating laboratories, the alkalinity results (when normalized to a common reference material) were in good agreement with each other and almost all data were within ±7 µmol/kg of the assigned value. This data quality is typical for laboratories with experience in this measurement, and indicates the increased experience the various participating laboratories have acquired over the past year.

Nevertheless, it is essential to maintain an awareness of potential inter-laboratory calibration problems, and the sources of these were discussed at length during the technical workshop. A full report, detailing both the 1999 and 2000 exercises is in preparation and should be completed in early 2001. The various workshop participants expressed an interest in continuing further such exercises on about a 2-year interval. We plan to explore ways of doing this in the future. In addition, Working Group 13 is planning an interlaboratory method comparison of the measurement of the $^{13}C/^{12}C$ ratio of the inorganic carbon in seawater for the coming year. This will involve the distribution of both a CO_2 gas samples, as well as a seawater samples. If you are interested in participating, please contact either Paul Quay (pdquay@u.washington.edu) or Andrew Dickson.

Participants of the second PICES CO_2 Technical Workshop in Tsukuba, Japan (October 20, 2000)

Country	**Affiliation**	**Name**
Canada	Institute of Ocean Sciences	Johnson, W. Keith
Japan	Frontier Research System, Japan	Ono, Tsuneo
	Hokkaido University	Nakano, Yoshiyuki
	Hokkaido University	Wakita, Masahide
	Hokkaido University	Watanabe, Shuichi
	Japan Marine Science and Technology Center	Murata, Akihiko
	Kansai Environmental Engineering Center Co. Ltd.	Ishida, Kazunori
	Kansai Environmental Engineering Center Co. Ltd.	Ota, Hidekazu
	Kansai Environmental Engineering Center Co. Ltd.	Tsubota, Hiroyuki
	Marine Works Japan Ltd.	Kitada, Makio
	Marine Works Japan Ltd.	Komai, Nobuharu
	Marine Works Japan Ltd.	Shibata, Fuyuki
	Meteorological Research Institute	Ishii, Masao
	National Institute for Resources and Environment	Harada, Koh
	National Institute for Resources and Environment	Tsurushima, Nobuo
	National Institute for Resources and Environment	Watanabe, Yutaka
	University of the Ryukyus	Fujimura, Hiroyuki
	Research Institute of Oceanochemistry, Osaka/Kimoto electric Co. Ltd.	Kimoto, Takashi
Korea	Seoul National University	Kang, Dong-Jin
Russia	Pacific Oceanological Institute, Vladivostok, Russia	Pavlova, Galina
USA	Atlantic Oceanographic and Meteorological Laboratory/NOAA	Lee, Kitack
	Scripps Institution of Oceanography	Afghan, Justine
	Scripps Institution of Oceanography	Dickson, Andrew
	University of Hawaii	Dore, John