

Distribution and Behaviors of Cd, Cu, and Ni in the East China Sea Surface Water off the Changjiang Estuary

Kuo-Tung Jiann^{1,*}, Liang-Saw Wen², and Gwo-Ching Gong^{3,4}

¹*Institute of Marine Geology and Chemistry, National Sun Yat-sen University, Kaohsiung 80424, Taiwan, ROC*

²*Institute of Oceanography, National Taiwan University, Taipei 10617, Taiwan, ROC*

³*Institute of Marine Environmental Chemistry and Ecology, National Taiwan Ocean University, Keelung 20224, Taiwan, ROC*

⁴*Taiwan Ocean Research Institute, National Applied Research Laboratories, Taipei 10622, Taiwan, ROC*

Received 27 December 2007, accepted 9 May 2008

ABSTRACT

Trace metal (Cd, Cu, and Ni) distributions and behaviors in surface waters of the East China Sea continental shelf were investigated during an expedition conducted in June 2004. Dissolved and particulate trace metal concentrations, as well as fractions of dissolved trace metals, fractionated based on their different chemical affinities to ion exchangers, were determined using ultra-clean techniques and graphite furnace atomic absorption spectrometry (GFAAS). Large variations of dissolved (< 0.45 m) metal concentrations in the East China Sea shelf waters were found (n = 16) and ranged between 0.036 - 0.287 nM for Cd, 0.87 - 8.66 nM for Cu, and 2.66 - 6.04 nM for Ni. Particulate metal contributions were highest near the river mouth. Dissolved Cd and Ni were predominantly present (98% for Cd and 86% for Ni) as Chelex-labile fractions in the shelf waters. The anionic-organic metal fractions accounted for, on average, 8% for Cu, < 1% for Cd, and 1% for Ni. The dissolved “inert” metal fractions, on average, were 32% for Cu, 2% for Cd, and 13% for Ni. Dissolved Cd, Cu, and Ni were linearly correlated with salinity and can be explained by a three or two-endmember mixing model. For Cu, all three dissolved fractions had inverse correlations with salinity and organic Cu accounted for a significant fraction of the total dissolved Cu suggesting that Cu is bioactive, but its association with biogeochemical processes in the shelf water was less important than mixing process.

Key words: Changjiang, East China Sea, Trace metals, Chemical affinity, Mixing

Citation: Jiann, K. T., L. S. Wen, and G. C. Gong, 2009: Distribution and behaviors of Cd, Cu, and Ni in the East China Sea surface water off the Changjiang Estuary. *Terr. Atmos. Ocean. Sci.*, 20, 433-443, doi: 10.3319/TAO.2008.05.09.01(Oc)

1. INTRODUCTION

Trace elements in the ocean have been classified into groups based on their biogeochemical reactivity (Bruland 1980). Cd, Cu, and Ni have been regarded as nutrient-type elements owing to their strong correlation with nutrients (N, P, or Si) down the water column in the oceans. In coastal and continental shelf waters, various processes affect trace metal distribution, including physical factors (water mass mixing and upwelling), external inputs (river, benthic and atmosphere) and biological processes (uptake, remineralization and export to deep ocean) (Achterberg et al. 1999; Le Gall et al. 1999; Cotte-Krief et al. 2002). However, specific trace elements behave differently depending on their variable chemical reactivity (e.g., Irvine-Williams Series for metal-

organic complexation). Therefore, in each aqueous compartment, processes involving trace metals occur at different degrees because of varying elemental reactivity and water chemistry (Honeyman and Santschi 1988; Santschi et al. 1997). When river plumes enter coastal areas, several important processes can affect trace metal partitioning, affinities, and removal. These include complexation with dissolved organic and inorganic ligands (Shine and Wallace 1995; Santschi et al. 1997), adsorption/desorption reactions with suspended and settling particles and plankton, flocculation and coagulation of colloids, humic substances and particulate matter, and remobilization from sediments (Sholkovitz 1978; Santschi et al. 1997; Wen et al. 1997).

In the East China Sea, the river plumes of the Changjiang, along with those of the Huanghe and the Minjiang, carry terrestrial materials and mix with the Kuroshio (Hsueh

* Corresponding author

E-mail: ktjiann@faculty.nsysu.edu.tw

2000) and the seasonally variable coastal current (Tsunogai et al. 2003). Furthermore, upwelling near the East China Sea continental slope transports subsurface water into the East China Sea continental shelf (Gong et al. 1995). In the continental shelf waters that may have either terrestrial or oceanic characteristics, different processes influence trace metal distributions. Therefore, trace metals in near-shore and shelf waters may have variable chemical affinities during the mixing process. The East China Sea is a marginal sea with multiple sources of water masses and especially with the dynamic flow of the river plume. Reliable data are required to elucidate distribution and behavior of trace elements, but studies in this area using clean methods are limited. Earlier works on water trace metals conducted in this region were mostly in the Chinese estuaries (Wang and Liu 2003; Koshikawa et al. 2007), including a review on China-US and China-French studies (Zhang 1995). Prior studies in this region mostly reported concentrations of one or two elements (Pai and Chen 1994; Noriki et al. 1998; Abe 2002). Therefore, trace metal distributions in the East China Sea warrant further investigation.

The present study, using clean techniques throughout the sampling, processing, and analytical procedures, is intended to provide information on the distribution and behavior of trace metals in this region. Dissolved metal fractions were fractionated based on their ion exchange chemical affinity that are essential for elucidating processes regarding trace metal biogeochemistry in waters collected off the Changjiang Estuary and its adjacent continental shelf waters. This paper is one of very few that reports not only multiple elements, but also results beyond total dissolved metal concentration in the vast East China Sea continental shelf.

2. MATERIAL AND METHODS

2.1 Sampling

Surface seawater samples from 16 locations in the East China Sea (Fig. 1) were collected during an expedition between 10 and 18 June 2004 on board R/V Ocean Researcher I. Rigorous clean sampling procedures were used throughout the sample collection and processing, as in previous studies (Wen et al. 1996; Wen et al. 1999). Polyethylene (PE) and PFA Teflon bottles were used for sampling, storage and sample processing. All bottles were acid washed thoroughly before use (Wen et al. 1996). Sampling bottles (2 L PE) were attached to a titanium rod with a polypropylene holder and lowered to ~50 cm depth from the bow of the ship upon arrival at the sampling locations. As soon as the 2-L bottles were filled and retrieved, they were transported to a class 100 clean bench on board. Thereafter, seawater samples were filtered immediately through a 0.45- μ m pore-sized acid-cleaned capsule filter (Osmonics, Westborough, MA, USA). At each sampling location, three 1-L aliquots

were collected. Two samples were filtered and one was not.

The sampling stations were arranged as three transects off the Changjiang Estuary and into the East China Sea (Lines B - D), and one across the northern Taiwan Strait (Line A) (Fig. 1). Line A (Stations 1 - 4) is between the Minjiang and the southernmost part of the Okinawa Trough, located off the coast of northeast Taiwan where the Kuroshio has a strong influence on water mixing and nutrient supply via upwelling. Lines B (Stations 15 - 18), C (Stations 27 - 29), and D (Stations 19 - 23) are located off the Changjiang river mouth.

All sample handling and manipulation was conducted in a class 100 laminar flow bench. While operating in the clean bench on board, one filtered sub-sample was immediately buffered by the addition of 20 mL of 1 M ammonia acetate solution (pH 5.5, made from doubly distilled acetic acid and ammonia solutions, both from Seastar, Baseline grade), and was subject to a dual-column ion exchange preconcentration procedure (Jiann and Presley 2002). The other filtered sample and the unfiltered sample were acidified (pH < 2) in the clean bench by adding 2 mL of sub-boiled nitric acid (Seastar, Baseline grade) into each sample (1 liter), and stored at 4 °C until being returned to the laboratory. In the land-based laboratory, the acidified samples in Teflon bottles were UV-digested (8 lamps of 15 W each) for 12 hours, in order to mobilize complexed and adsorbed trace metals (Wen et al. 1996; Achterberg et al. 2001).

2.2 Trace Metal Analysis

In this study, we used a fractionation procedure that utilized a cationic exchange column (resin: Chelex-100, 100 -

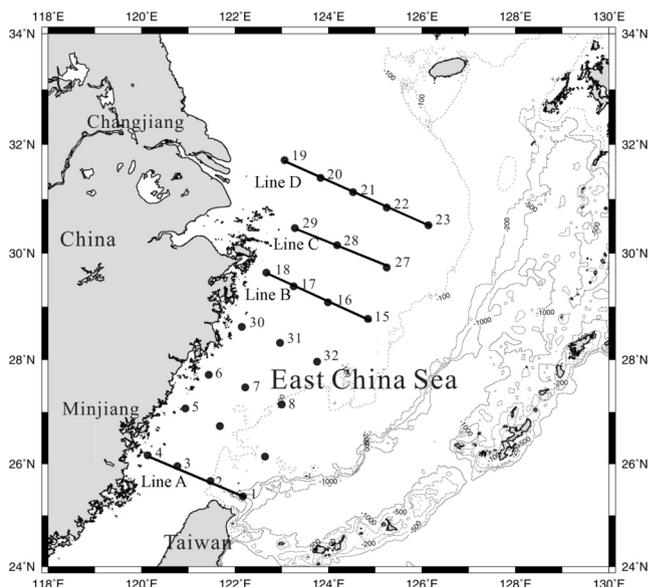


Fig. 1. Regional map of the East China Sea with sampling locations indicated.

200 mesh, ammonia form, Bio-Rad; column: Poly-Prep, Bio-Rad) to obtain Chelex-labile metal fractions (Donat et al. 1994; Shafer et al. 2004) and an anionic exchange column (AG MP1 resin, 100 - 200 mesh, OH⁻ form, Bio-Rad), connected in series, to further differentiate anionic-organic and inert fractions (Jiann and Presley 2002). Briefly, dissolved trace metal fractions are separated according to their ion exchange affinity and fractionated into Chelex-labile (ionic and weakly bound complex forms), anionic-organic (humic-like anionic-organic complexes), and inert (strongly bound complexes or minerals) fractions. Detailed concepts and fractionation designs are described by Jiann and Presley (2002). Although the fractionation technique is operational in nature, it has been successfully applied in river (Shiller et al. 2006), estuarine (Jiann et al. 2005), and oceanic (Wen et al. 2006) environments to elucidate biogeochemical processes involving trace metals. Processes such as the redistribution of metal fractions caused by photo-oxidation of dissolved organic matter (Shiller et al. 2006), the presence of metal-sulfide minerals in suboxic and anoxic waters (Jiann et al. 2005), and distribution of metal fractions and their reactivity in an oligotrophic ocean (Wen et al. 2006) have been revealed using this technique.

Immediately after collection, samples were passed through the column sets at a flow rate of 2 - 3 mL min⁻¹ and pH ~5.5 in a class 100 clean bench. After the passage of samples, the columns were disconnected. Following a washing step to separate major cations from the columns, metals of interest were eluted with 2 N nitric acid (Seastar, Baseline doubly distilled grade) for subsequent assay. Total dissolved metal concentrations were determined on separate filtered samples that had been acidified and UV-digested, after pre-concentrating metals on Chelex-100 columns. The dissolved inert metal fraction (not retained by either Chelex-100 or AG MP1 column) was obtained as the difference between total dissolved metal concentration and the sum of Chelex-labile and anionic-organic metal concentrations. Total metal concentrations were obtained from unfiltered samples that were UV-digested after acidification, and pre-concentrated. Particulate metal concentrations were calculated from the differences between total concentrations (unfiltered samples) and total dissolved concentrations (filtered samples). Measurement of trace metal concentration was performed on a graphite furnace atomic absorption spectrometer (GFAAS, Varian, SpectrAA 880Z), equipped with an auto-sampler and a Zeeman correction system. Accuracy of the pre-concentration procedure was confirmed by processing seawater standard reference materials (CASS 4 and NASS 5, both from the National Research Council of Canada); the recoveries of metals determined for the two reference materials were 88 - 112%. Precision was 2 - 5% for the metals analyzed, estimated from replicate samples of ambient concentrations. Detection limits for each trace metal fractions were estimated from 3 times standard deviations of their

replicate blank concentrations. They are: Cd, 0.001 nM; Cu, 0.02 - 0.05 nM; Ni, 0.02 - 0.06 nM.

2.3 Supporting Data

At each sampling location, temperature, salinity, and fluorescence profiles were obtained with a Seabird CTD (SBE-11, General Oceanics) attached to a rosette sampler. Discrete water samples were collected using 10-L X-Niskin (General Oceanics) bottles and aliquots of samples were taken for nutrient (nitrite, nitrate, phosphate, and silicate) and chlorophyll *a* measurements. Determination of nitrite and nitrate was made by using the standard pink azo dye method modified for a flow injection analyzer (Pai et al. 1990a). Phosphate and silicate were determined using molybdenum blue spectrophotometric method on a flow injection analyzer (Pai et al. 1990b). Samples for chlorophyll *a* determination were filtered immediately through GF/F filters (25 mm, Whatman), stored at -20 °C, and later analyzed on a fluorometer (10-AU-005, Turner) following the method described by Strickland and Parsons (1972).

3. RESULTS AND DISCUSSION

3.1 Hydrography

Distribution of salinity in surface waters (Table 1) of the East China Sea continental shelf during our sampling period is shown in Fig. 2. Salinity ranged from 30.1 near the Changjiang river mouth to 34.6 at the southeast continental slope (Station 1). It is clear that during the sampling period, the Changjiang discharge predominantly extended towards the east and northeast on the continental shelf, as high salinity water penetrated from southeast into our sampling transects. This should cause higher salinity at Station 28 than at surrounding stations (Fig. 2). In general, the stations closest to the shoreline of China (4, 18, 19, and 29) had the highest nutrient concentrations (Table 1). Nitrite concentrations ranged from 0.10 ~ 0.68 μM at near-shore stations to below 0.04 μM in the shelf waters. Nitrate concentrations ranged from 0.64 to 9.40 μM in the near-shore waters and were < 0.40 μM in the shelf waters. Silicate was slightly higher (10.2 - 12.5 μM) at near-shore stations (18, 19, 20, and 29) and was between 1.9 and 7.6 μM in the shelf waters. Phosphate in the East China Sea surface waters ranged between 0.06 and 0.15 μM. Distributions of nutrients in the East China Sea shelf waters did not show apparent river-ocean mixing as no decreasing trends going seaward were found in each transect. Higher chlorophyll *a* concentrations were found at stations near the Changjiang river mouth (Stations 18, 19, 28, and 29). In addition, elevated chlorophyll *a* concentration was also observed at a known upwelling location (Station 1) where phosphate concentrations were found to be higher than those in surrounding waters. Earlier studies have shown that nutrients supplied from the Changjiang influx

Table 1. Sampling locations, sampling times, hydrology, and nutrient data for the East China Sea shelf waters sampled in June, 2004.

Station	Longitude (°E)	Latitude (°N)	Date	Time	Sigma-theta (°C)	Salinity psu	Nitrite μM	Nitrate μM	Phosphate μM	Silicate μM	Chlorophyll a mg m ⁻³
1	122.21	25.42	2004/6/11	14:00	23.271	34.558	0.02	0.37	0.10	1.9	1.153
2	121.50	25.67	2004/6/11	19:30	22.502	34.369	0.00	0.40	0.06	2.8	0.407
3	120.79	25.92	2004/6/12	01:00	22.813	34.139	0.02	0.38	0.06	2.7	0.579
4	120.08	26.17	2004/6/12	06:00	22.402	33.273	0.68	0.64	0.10	3.8	0.736
15	124.90	28.71	2004/6/16	06:30	22.671	33.870	0.02	0.35	0.10	3.8	0.390
16	124.13	29.00	2004/6/16	01:00	22.879	34.512	0.00	0.28	0.10	2.3	0.262
17	123.37	29.30	2004/6/15	19:45	22.958	34.455	0.01	0.19	0.10	2.8	0.489
18	122.67	29.54	2004/6/13	10:00	20.560	30.136	0.47	9.40	0.15	12.5	2.410
19	123.15	31.62	2004/6/14	00:40	21.034	31.083	0.10	2.35	0.12	10.7	0.940
20	123.91	31.33	2004/6/14	06:00	21.224	31.450	0.03	0.00	0.13	3.7	1.091
21	124.70	31.04	2004/6/14	10:48	22.138	32.434	0.02	0.01	0.08	4.5	0.563
22	125.46	30.75	2004/6/14	15:45	22.275	32.650	0.02	0.09	0.08	7.6	0.354
23	126.23	30.46	2004/6/14	21:30	22.503	33.227	0.01	0.10	0.08	5.2	0.177
27	125.31	29.68	2004/6/15	05:00	21.341	31.595	0.02	0.09	0.09	6.5	0.419
28	124.28	30.07	2004/6/15	12:30	22.335	33.188	0.04	0.14	0.15	2.9	1.950
29	123.25	30.45	2006/6/13	17:15	21.147	31.445	0.11	1.93	0.12	10.2	0.907

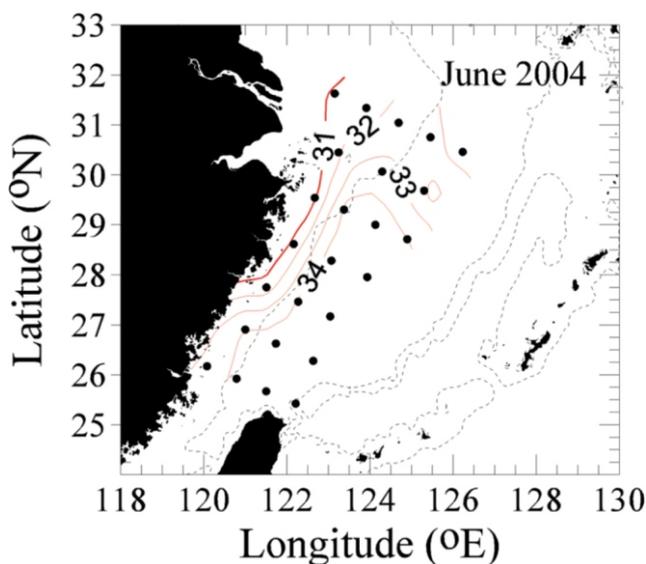


Fig. 2. Salinity structure of the surface water on the East China Sea continental shelf, surveyed during 10 - 18 June 2004.

are recycled quickly and reused on the East China Sea continental shelf to result in higher primary production near the coastal and estuarine regions (Gong et al. 2003; Shin et al. 2003; Tsunogai et al. 2003). Our results are in concert with these earlier findings.

3.2 Distribution of Total Dissolved and Particulate Trace Metals

Results of total dissolved (< 0.45 μm) and particulate trace metal concentrations at each location are listed in Table 2. Of the three elements analyzed, dissolved Cd and Cu showed large spatial variations, with the concentration varying as much as a factor of 8 - 10 (Cd: 0.036 - 0.287 nM; Cu: 0.87 - 8.67 nM), while total dissolved Ni fell into narrower concentration ranges (2.66 - 6.04 nM). Dissolved metal concentrations in the surface waters of high salinity (Stations 1, 2, 16, and 17) were found to be much lower than those at stations in the rest of the study area (Table 2). In the outer shelf and slope areas, dissolved Cu concentrations were slightly higher than those reported for waters collected in the same geographic area (Abe et al. 2003). Our dissolved Cd concentrations were higher than those in surface water over the slope regions (Pai and Chen 1994; Abe, 2002). The observed differences could be attributed to a few reasons. First, there could be temporal variations of the input (endmember concentration) from the Changjiang. Compared with dissolved metal concentrations in the Changjiang Estuary at salinity 19 reported by Wang and Liu (2003) as the following: Cu and Ni, ~20 nM; and Cd, 0.36 nM, our results are much lower. Compared with a more recent Changjiang Estuary data set of water salinity 30 - 34, of which dissolved

Table 2. Total dissolved and particulate trace metal concentrations in the East China Sea shelf waters collected in June, 2004.

Station	Cd				Cu				Ni			
	Dissolved		Particulate		Dissolved		Particulate		Dissolved		Particulate	
	nM	%	nM	%	nM	%	nM	%	nM	%	nM	%
1	0.039	91	0.004	9	0.87	93	0.06	7	2.66	98	0.04	2
2	0.036	88	0.005	12	1.56	83	0.33	17	2.91	98	0.07	2
3	0.062	95	0.003	5	2.18	87	0.33	13	3.60	99	0.04	1
4	0.113	83	0.023	17	4.61	83	0.97	17	4.18	87	0.60	13
15	0.066	95	0.004	5	2.25	91	0.22	9	3.29	96	0.12	4
16	0.036	89	0.004	11	1.45	89	0.18	11	2.73	94	0.17	6
17	0.043	90	0.005	10	1.56	96	0.07	4	2.75	95	0.16	5
18	0.287	67	0.141	33	8.66	84	1.60	16	6.04	93	0.48	7
19	0.131	71	0.054	29	6.19	81	1.41	19	5.01	97	0.15	3
20	0.124	71	0.051	29	5.45	80	1.36	20	4.73	96	0.18	4
21	0.143	86	0.023	14	4.54	91	0.44	9	3.90	95	0.19	5
22	0.144	90	0.016	10	4.10	91	0.41	9	4.07	99	0.04	1
23	0.128	94	0.009	6	3.32	91	0.31	9	3.72	98	0.09	2
27	0.110	89	0.013	11	5.50	89	0.70	11	4.58	98	0.10	2
28	0.091	96	0.004	4	3.19	87	0.48	13	3.84	99	0.04	1
29	0.144	69	0.064	31	6.32	84	1.23	16	5.35	98	0.12	2
Average	0.106	85	0.026	15	3.86	87	0.63	13	3.96	96	0.16	4

metal concentrations were Cd, 0.1 - 0.6 nM; Cu, 3 nM; and Ni, 4 - 9 nM (Koshikawa et al. 2007), our results are comparable with theirs. Second, studies have shown that colloids often sequester analytes that must be destroyed by appropriate treatment prior to analysis (Ostapczuk 1993; Wen et al. 1999; Achterberg et al. 2001). Earlier results in the East China Sea and northwestern Pacific marginal seas were mostly obtained without a UV-digestion procedure prior to determination of total dissolved trace metals. Therefore those reported values could have been underestimated. A comparison of dissolved trace metal concentrations in the region (Table 3) shows that, when salinity difference is considered, results of metal concentrations are comparable. Higher concentrations were only observed in river and estuarine waters (Zhang 1995; Wang and Liu 2003; Koshikawa et al. 2007) which were affected by varying river end-member concentrations. The concentrations we observed in the shelf and coastal waters away from river mouth are similar to those obtained from shelf waters in the region.

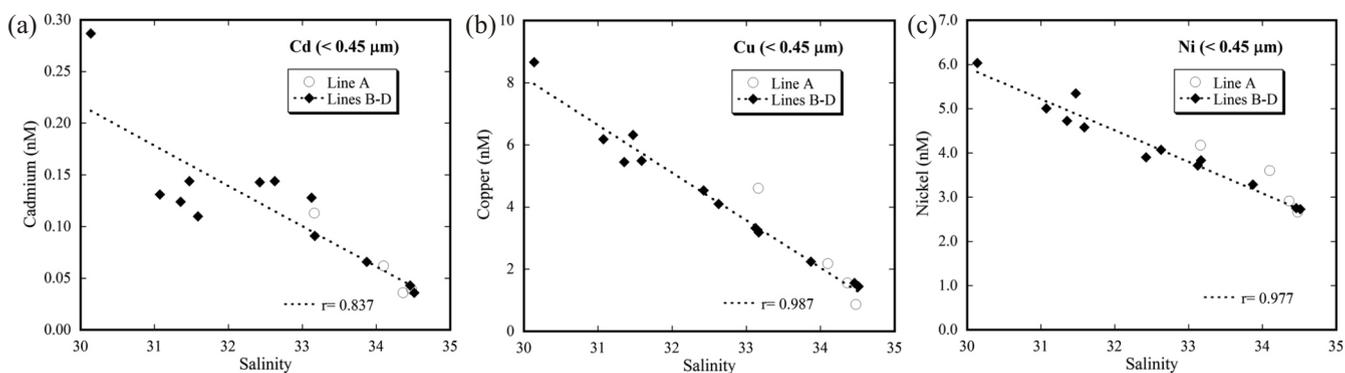
Dissolved Cu and Ni, and to a less extent, Cd, showed conservative mixing behavior for surface waters of the entire East China Sea shelf (Fig. 3). As shown in other studies, distributions of Cu and Ni in coastal surface seawater were

affected mostly by mixing between river and oceanic waters (Achterberg et al. 1999; Le Gall et al. 1999; Abe et al. 2003). Both hydrographic (Fig. 2) and trace metal data indicated that there was a northeastward plume from the Changjiang, with oceanic water penetrating across the shelf and into our survey transects (B - D). The southeastern portion of the study area had higher salinity and lower metal concentrations (Table 2). Correlations between dissolved metal concentration and salinity for Line A are apparently different from those of Lines B - D. However, the small sample number did not allow us to further elaborate on their differences.

Particulate metals were much higher at near-shore locations (Stations 4, 18, 19, 20, and 29; Table 2) and decreased seaward. The lowest particulate metal concentrations were found in the slope water (Station 1). Cd had varying particulate fractions, ranging from 20% to 30% in near-shore waters to 5 - 10% in shelf and slope waters. On average, particulate Cd accounted for 15% of total Cd concentration in the surface waters. The average particulate Cu fraction was 13% relative to total Cu concentration. Among the three elements determined, Ni had the lowest, yet constant, particulate fraction relative to total Ni concentration, accounting for less than 7% of total Ni, except for one sample collected near the

Table 3. Comparison of dissolved trace metal concentrations in the East China Sea continental shelf and its adjacent estuary/sea.

Sea/ocean	Salinity	Cd	Cu	Ni	Reference
		nM	nM	nM	
Western North Pacific	34.4		2.4	1.9	Noriki et al. 1998
Sea of Okhotsk	32.4	0.09			Abe 2002
Okinawa Trough	34.5	< 0.04			Pai and Chen 1994
Changjiang Estuary	19	0.36	20	22	Wang and Liu 2003
Changjiang Estuary	30 - 34	0.1 - 0.6	3	4 - 9	Koshikawa et al. 2007
Changjiang Estuary	33	0.16	5		Zhang 1995
Minjiang Estuary	33	0.08	4		Zhang 1995
East China Sea	24 - 34		0.58 - 9.37		Abe et al. 2003
East China Sea	30.1-34.6	0.036 - 0.287	0.87 - 8.66	2.66 - 6.04	This study

Fig. 3. Relationship between total dissolved trace metal concentration (< 0.45 μ m filter-passing) and salinity in the East China Sea shelf waters.

Minjiang river mouth (Station 4, 13%). Particulate metal concentrations obtained in this study (Table 2) are comparable with those reported for shelf water off the Changjiang Estuary (Zhang and Liu 2002; Koshikawa et al. 2007).

3.3 Distribution of Dissolved Trace Metal Fractions

Results of dissolved concentration of different chemical affinity fractions are shown in Table 4. Dissolved Cd existed mostly in the labile fraction, with only ~2% in the inert fraction. The only noticeable dissolved inert Cd (0.01 nM, or 4% of total dissolved Cd) was observed at Station 18, the location closest to the Changjiang river mouth with the lowest salinity. The high percentage of Chelex-labile Cd indicates that, upon reaching the coast, Cd is present as labile species, most likely in the forms of chloride complexes (Jiann et al. 2005; Wen et al. 2006).

On average, the Chelex-labile, anionic-organic and inert Cu fractions accounted for 58, 8, and 34%, respectively, of

the total dissolved Cu. The anionic-organic Cu fraction was consistently low, accounting for 1 - 10% of total dissolved Cu. Inert Cu fraction was elevated in the high salinity waters (up to 58%) in which the Chelex-labile Cu fraction was low (34%). All dissolved Cu fractions showed conservative mixing behavior in the East China Sea shelf waters (Fig. 4).

Dissolved Ni was also predominantly in the Chelex-labile fraction (Table 4), accounting for 83 - 90% of total dissolved Ni. Anionic-organic Ni fractions accounted for a minor proportion (< 4% of the total dissolved Ni). For the inert Ni fraction, a relatively constant percentage (10 - 16%) was found. The anionic-organic Ni fractions did not show clear distribution patterns, while the inert Ni fractions were higher in the near-shore waters (Stations 4, 18, 19, and 29), averaging 0.72 nM (0.52 - 0.81) compared to 0.43 nM (0.31 - 0.61) in shelf waters. The relatively constant dissolved Chelex-labile and inert Ni fractions (%) indicate that they behave conservatively in the shelf water, like the trend of total dissolved Ni (Fig. 3).

Table 4. Dissolved trace metal fractions (concentration in nM and percentage relative to total dissolved concentration, concentrations below detection limits are indicated as < detection limit) in the East China Sea continental shelf waters collected in June, 2004.

Station	Salinity	Cd			Cu			Ni											
		Chelexlabile %	Anionicorganic %	Inert %	Chelexlabile %	Anionicorganic %	Inert %	Chelexlabile %	Anionicorganic %	Inert %									
1	34.558	0.038	97	<0.001	0	0.001	3	0.30	34	0.07	8	0.51	58	2.24	84	0.10	4	0.32	12
2	34.369	0.035	97	<0.001	0	0.001	3	0.85	55	0.11	7	0.60	38	2.54	87	0.06	2	0.31	11
3	34.139	0.060	97	<0.001	0	0.002	3	1.10	50	0.20	9	0.88	40	3.20	89	<0.06	1	0.35	10
4	33.273	0.112	99	<0.001	0	0.001	1	2.40	52	0.43	9	1.78	39	3.54	85	0.11	3	0.52	13
15	33.870	0.065	98	<0.001	0	0.001	2	1.38	61	0.14	6	0.72	32	2.77	84	<0.06	0	0.52	16
16	34.512	0.035	97	<0.001	0	0.001	3	0.86	59	0.02	1	0.57	39	2.37	87	<0.06	0	0.36	13
17	34.455	0.042	98	<0.001	0	0.001	2	0.86	55	0.09	6	0.61	39	2.34	85	<0.06	0	0.41	15
18	30.136	0.277	97	<0.001	0	0.010	3	5.12	59	0.84	10	2.70	31	5.28	87	<0.06	0	0.75	12
19	31.083	0.130	99	<0.001	0	0.001	1	3.50	57	0.62	10	2.07	33	4.18	83	<0.06	0	0.81	16
20	31.450	0.122	98	<0.001	0	0.002	2	3.32	61	0.47	9	1.66	30	4.11	87	0.07	1	0.56	12
21	32.434	0.140	98	<0.001	0	0.003	2	2.84	63	0.34	8	1.36	30	3.45	88	<0.06	1	0.42	11
22	32.650	0.141	98	<0.001	0	0.003	2	2.63	64	0.31	8	1.16	28	3.44	84	<0.06	1	0.61	15
23	33.227	0.125	98	<0.001	0	0.003	2	2.27	68	0.23	7	0.82	25	3.20	86	0.07	2	0.45	12
27	31.595	0.108	98	<0.001	0	0.002	2	3.64	66	0.41	7	1.45	26	4.13	90	<0.06	0	0.44	10
28	33.188	0.090	98	<0.001	0	0.002	2	2.03	64	0.27	8	0.89	28	3.36	88	<0.06	0	0.47	12
29	31.445	0.142	99	<0.001	0	0.002	1	3.70	58	0.52	8	2.11	33	4.55	85	<0.06	0	0.80	15
Average			98		0	0	2		58		8		34		86		1		13

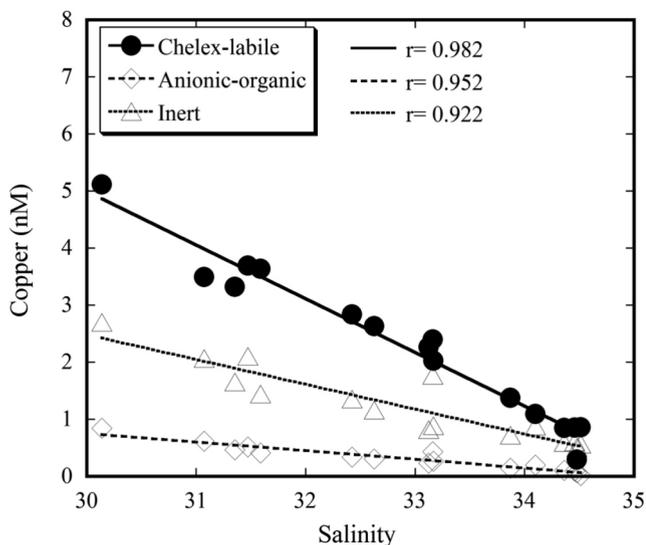


Fig. 4. Relationship between dissolved Cu fractions and salinity. All 3 dissolved Cu fractions had strong correlation with salinity, suggesting mixing-dominant effect.

The presence of non-labile metal fractions calls for special attention when regional datasets are compared. As mentioned earlier, natural water samples analyzed without digestion procedure may underestimate their trace metal concentrations. For dissolved trace metal fractions in the East China Sea shelf waters, Cd and Ni have a very small amount of anionic-organic and inert fractions, while all three dissolved fractions of Cu accounted for important proportions.

3.4 Distribution and Behavior of Trace Metals

Both dissolved and particulate metal concentrations, as well as chlorophyll *a* and most nutrient concentrations, were higher in waters near the Changjiang river mouth, indicating elevated terrestrial influence in the Changjiang Estuary (Tables 1 and 2). However, correlations between metal and silicate (or chlorophyll *a*) concentrations in Lines B - D

(Fig. 5) should not be ascribed solely to the association of trace metals with biological activity. Considering that all three dissolved Cu fractions, as well as those of Ni, correlated well with salinity, it is suggested that trace metal distributions in the East China Sea shelf waters off the Changjiang Estuary were predominantly controlled by mixing. The outliers in the dissolved Cd-salinity plot are from Stations 19, 20, 27, and 29 (Fig. 3) which are located directly off the Changjiang river mouth, except that Stations 27 and 29 were separated by the penetration of oceanic water. Stations 18 and 21 - 23 belong to another group of locations with Cd-salinity relationship, and are located further away from the river mouth. Therefore, the mixing process in the study area during our sampling period appeared to be a three-end-member case off the Changjiang Estuary since two distinct correlations can be derived from the Cd-Cu plot, as illustrated in Fig. 5. These different correlations resulted from variability of endmember concentrations between the two groups of locations mentioned above. Based on that the samples were collected within 1 - 2 days for each group of the locations (Table 1), it is suggested that the Changjiang endmember concentrations varied on the time scale of 1 - 2 days for Cd, while they were constant for Cu and Ni over 4 - 5 days. Furthermore, no correlation can be established between Cd and phosphate, or nitrate, like the uptake-regeneration model normally observed in the open ocean. Silicate showed positive linear correlation with Cu (Fig. 5) with a higher degree of scattering ($r = 0.864$), suggesting that silicate export from the Changjiang was temporally variable.

Among the three elements determined in this study, only Cu had substantial organic fractions in the dissolved pools, probably suggesting strong association with biological processes and/or organic complexation. Higher dissolved anionic-organic Cu fractions were observed at stations closer to the coast, where chlorophyll *a* concentrations were also higher. Good correlations between dissolved Cu fractions and salinity indicate conservative mixing behavior of Cu in the East China Sea continental shelf waters. It is therefore suggested that the organic complexation of Cu occurred

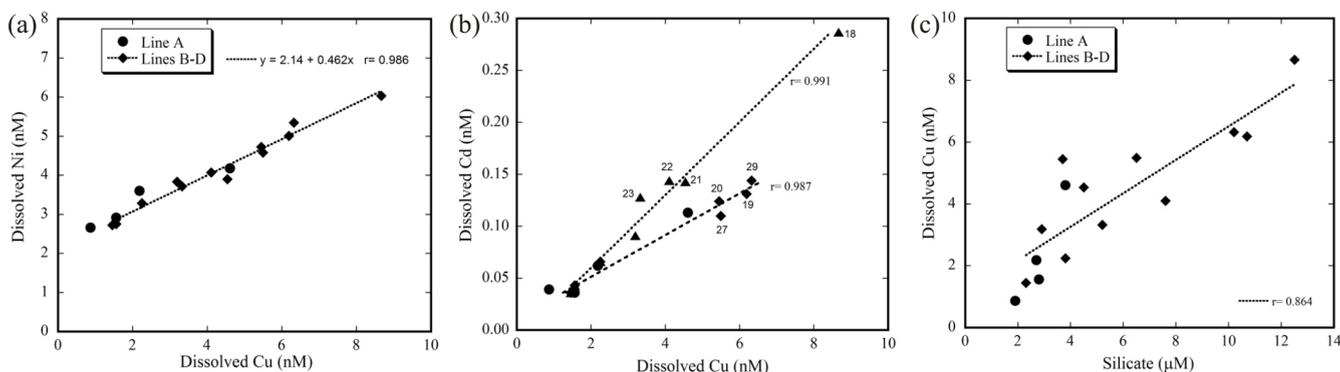


Fig. 5. Relationship between: (a) dissolved Ni and Cu, (b) dissolved Cd and Cu, and (c) dissolved Cu and silicate.

above or near the Changjiang river mouth, and mixing dominated in the continental shelf waters. Therefore, the association with terrestrial humic substances was likely the major cause for the observed anionic-organic Cu fractions in the shelf waters. Our results reveal that the nature of the anionic-organic and inert metal fractions were terrestrial, since the presence of humic substance can contribute to metal complexation (Buffle 1988) which would have organic characteristics, but can be kinetically inert (Kogut and Voelker 2003) in coastal waters. The presence of relatively constant anionic-organic Cu fractions (%) in the surface waters were in concert with similar findings observed in French coastal waters, where constant hydrophobic Cu fractions were reported (Waeles et al. 2004), and in the Narragansett Bay, USA (salinity 25 - 30), where colloidal (1 - 8 kDa) Cu behaved near conservatively in the estuary (Wells et al. 2000). These findings, combined with the observations of the linear relationship between dissolved metal fractions and salinity, suggest that, in the East China Sea, biological activities involving trace metals and redistribution of metal fractions are not as significant as mixing process.

4 CONCLUSION

Dissolved trace metal concentrations in the waters off the Changjiang Estuary and along the continent shelf obtained in this study are consistent with previously reported values. The distributions of Cd, Cu, and Ni in the East China Sea continental shelf waters were affected predominantly by mixing between source waters from the Changjiang (and the Minjiang) and oceanic water masses. Based on the observations of (1) particulate metal concentrations decreasing eastward along each transect and (2) the presence of higher anionic-organic and/or inert metal fractions in waters off the Changjiang Estuary and their dilution on the continental shelf, it is suggested that there are substantial terrestrial influence of trace metals in the East China Sea continental shelf. These strongly bound or complexed metal fractions were present within the estuary before reaching the shelf water.

In addition to conventional dissolved and particulate metal concentrations, the partition of trace metals in various chemical forms are reported in the East China Sea continental shelf waters. The percentages of the Chelex-labile metal fractions were in the order: Cd > Ni > Cu, the anionic-organic fractions: Cu > Ni > Cd, and the inert fractions: Cu > Ni > Cd. The observed low organic and inert fractions for Cd and Ni, along with the presence of linear relationships between all three dissolved Cu fractions with salinity, indicate that biogeochemical processes involving the distribution of the three metals occur mostly within the Changjiang Estuary. The organic and inert fractions of Cu are present at significant proportions within the Changjiang Estuary as they became organically complexed in the riverine and estuarine

regions and are progressively diluted on the East China Sea shelf.

Acknowledgements The authors would like to thank the captain and crew of the R/V Ocean Researcher I of National Taiwan University and technical assistants Ms. Hsiu-Ping Li and Mr. Han-Song Ong of the National Center for Ocean Research (NCOR) for their assistance during the sampling cruise. Three anonymous reviewers provided constructive comments that greatly helped to strengthen the manuscript. This study was financially supported by the National Science Council of Taiwan through research grants NSC 92-2611-M-002-016, 94-2611-M-002-023. This work was also in part supported by the Center for Marine Bioscience and Biotechnology, National Taiwan Ocean University.

REFERENCES

- Abe, K., 2002: Performed Cd and PO₄ and the relationship between the two elements in the northwestern Pacific and the Okhotsk Sea. *Mar. Chem.*, **79**, 27-36, doi: 10.1016/S0304-4203(02)00038-5. [[Link](#)]
- Abe, K., Y. Ishihi, and Y. Watanabe, 2003: Dissolved copper in the Yellow Sea and the East China Sea - Cu as a tracer of the Changjiang discharge. *Deep-Sea Res. II*, **50**, 327-337, doi: 10.1016/S0967-0645(02)00457-5. [[Link](#)]
- Achterberg, E. P., C. Colombo, and C. M. G. van den Berg, 1999: The distribution of dissolved Cu, Zn, Ni, Co and Cr in English coastal surface waters. *Cont. Shelf Res.*, **19**, 537-558, doi: 10.1016/S0278-4343(98)00093-4. [[Link](#)]
- Achterberg, E. P., C. B. Braungardt, R. C. Sandford, and P. J. Worsfold, 2001: UV digestion of seawater samples prior to the determination of copper using flow injection with chemiluminescence detection. *Anal. Chim. Acta*, **440**, 27-36, doi: 10.1016/S0003-2670(01)00824-8. [[Link](#)]
- Bruland, K. W., 1980: Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific. *Earth Planet. Sc. Lett.*, **47**, 176-198, doi: 10.1016/0012-821X(80)90035-7. [[Link](#)]
- Buffle, J., 1988: Complexation Reactions in Aquatic Systems: An Analytical Approach. John Wiley & Sons, New York, 692 pp.
- Cotte-Krief, M. H., A. J. Thomas, and J. M. Martin, 2002: Trace metal (Cd, Cu, Ni and Pb) cycling in the upper water column near the shelf edge of the European continental margin (Celtic Sea). *Mar. Chem.*, **79**, 1-26, doi: 10.1016/S0304-4203(02)00013-0. [[Link](#)]
- Donat, J. R., K. A. Lao, and K. W. Bruland, 1994: Speciation of dissolved copper and nickel in South San Francisco Bay: A multi-method approach. *Anal. Chim. Acta*, **284**, 547-571, doi: 10.1016/0003-2670(94)85061-5. [[Link](#)]
- Gong, G. C., K. K. Liu, and S. C. Pai, 1995: Prediction of nitrate concentration from two end member mixing in the southern East China Sea. *Cont. Shelf Res.*, **15**, 827-842, doi:

- 10.1016/0278-4343(94)00039-P. [[Link](#)]
- Gong, G. C., Y. H. Wen, B. W. Wang, and G. J. Liu, 2003: Seasonal variation of chlorophyll a concentration, primary production and environmental conditions in the subtropical East China Sea. *Deep-Sea Res. II*, **50**, 1219-1236, doi: 10.1016/S0967-0645(03)00019-5. [[Link](#)]
- Honeyman, B. D. and P. H. Santschi, 1988: Metals in aquatic systems. *Environ. Sci. Technol.*, **22**, 862-871, doi: 10.1021/es00173a002. [[Link](#)]
- Hsueh, Y., 2000: The Kuroshio in the East China Sea. *J. Marine Syst.*, **24**, 131-139, doi: 10.1016/S0924-7963(99)00083-4. [[Link](#)]
- Jiann, K. T. and B. J. Presley, 2002: Preservation and determination of trace metal partitioning in river water by a two-column ion exchange method. *Anal. Chem.*, **74**, 4716-4724, doi: 10.1021/ac025626h. [[Link](#)]
- Jiann, K. T., L. S. Wen, and P. H. Santschi, 2005: Trace metal (Cd, Cu, Ni and Pb) partitioning, affinities and removal in the Danshuei River estuary, a macro-tidal, temporally anoxic estuary in Taiwan. *Mar. Chem.*, **96**, 293-313, doi: 10.1016/j.marchem.2005.03.001. [[Link](#)]
- Kogut, M. B. and B. M. Voelker, 2003: Kinetically inert Cu in coastal waters. *Environ. Sci. Technol.*, **37**, 509-519, doi: 10.1021/es020723d. [[Link](#)]
- Koshikawa, M. K., T. Takamatsu, J. Takada, M. Zhu, B. Xu, Z. Chen, S. Murakami, K. Xu, and M. Watanabe, 2007: Distributions of dissolved and particulate elements in the Yangtze estuary in 1997-2002: Background data before the closure of the Three Gorges Dam. *Estuar. Coast. Shelf Sci.*, **71**, 26-36, doi: 10.1016/j.ecss.2006.08.010. [[Link](#)]
- Le Gall, A. C., P. J. Statham, N. H. Morley, D. J. Hydes, and C. H. Hunt, 1999: Processes influencing distributions and concentrations of Cd, Cu, Mn and Ni at the North West European shelf break. *Mar. Chem.*, **68**, 97-115, doi: 10.1016/S0304-4203(99)00068-7. [[Link](#)]
- Noriki, S., Y. Arashitani, M. Minakawa, K. Harada, and S. Tsunogai, 1998: Vertical cycling of Cu and Ni in the western North and Equatorial Pacific. *Mar. Chem.*, **59**, 211-218, doi: 10.1016/S0304-4203(97)00098-4. [[Link](#)]
- Ostapczuk, P., 1993: Present potentials and limitations in the determination of trace elements by potentiometric stripping analysis. *Anal. Chim. Acta*, **273**, 35-40, doi: 10.1016/0003-2670(93)80142-8. [[Link](#)]
- Pai, S. C. and H. Y. Chen, 1994: Vertical distribution of cadmium in marginal seas of the western Pacific Ocean. *Mar. Chem.*, **47**, 81-91, doi: 10.1016/0304-4203(94)90015-9. [[Link](#)]
- Pai, S. C., C. C. Yang, and J. P. Riley, 1990a: Formation kinetics of the pink azo dye in the determination of nitrite in natural waters. *Anal. Chim. Acta*, **232**, 345-349, doi: 10.1016/S0003-2670(00)81252-0. [[Link](#)]
- Pai, S. C., C. C. Yang, and J. P. Riley, 1990b: Effects of acidity and molybdate concentration on the kinetics of the formation of the phosphoantimonylmolybdenum blue complex. *Anal. Chim. Acta*, **229**, 115-120, doi: 10.1016/S0003-2670(00)85116-8. [[Link](#)]
- Santschi, P. H., J. J. Lenhart, and B. D. Honeyman, 1997: Heterogeneous processes affecting trace contaminant distribution in estuaries: The role of natural organic matter. *Mar. Chem.*, **58**, 99-125, doi: 10.1016/S0304-4203(97)00029-7. [[Link](#)]
- Shafer, M. M., S. R. Hoffmann, J. T. Overdier, and D. E. Armstrong, 2004: Physical and kinetic speciation of copper and zinc in three geochemically contrasting marine estuaries. *Environ. Sci. Technol.*, **38**, 3810-3819, doi: 10.1021/es0306765. [[Link](#)]
- Shiller, A. M., S. Duan, P. van Erp, and T. S. Bianchi, 2006: Photo-oxidation of dissolved organic matter in river water and its effect on trace element speciation. *Limnol. Oceanogr.*, **51**, 1716-1728.
- Shin, K. H., T. Hama, and N. Handa, 2003: Effect of nutrient conditions on the composition of photosynthetic products in the East China Sea and surrounding waters. *Deep-Sea Res. II*, **50**, 389-401, doi: 10.1016/S0967-0645(02)00463-0. [[Link](#)]
- Shine, J. P. and G. T. Wallace, 1995: The formation of surface-active organic complexes of copper in coastal marine waters. *Mar. Chem.*, **51**, 145-157, doi: 10.1016/0304-4203(95)00050-2. [[Link](#)]
- Sholkovitz, E. R., 1978: The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co and Cd during estuarine mixing. *Earth Planet. Sc. Lett.*, **41**, 77-86, doi: 10.1016/0012-821X(78)90043-2. [[Link](#)]
- Strickland, J. D. H. and T. R. Parsons, 1972: A Practical Handbook of Seawater Analysis. Fisheries Research Board of Canada, Ottawa, Canada, 310 pp.
- Tsunogai, S., K. Iseki, M. Kusakabe, and Y. Saito, 2003: Biogeochemical cycles in the East China Sea: MASFLEX program. *Deep-Sea Res. II*, **50**, 321-326, doi: 10.1016/S0967-0645(02)00456-3. [[Link](#)]
- Waeles, M., R. D. Riso, J. F. Maguer, and P. Le Corre, 2004: Distribution and chemical speciation of dissolved cadmium and copper in the Loire estuary and North Biscay continental shelf, France. *Estuar. Coast. Shelf Sci.*, **59**, 49-57, doi: 10.1016/j.ecss.2003.07.009. [[Link](#)]
- Wang, Z. L. and C. Q. Liu, 2003: Distribution and partition behavior of heavy metals between dissolved and acid-soluble fractions along a salinity gradient in the Changjiang Estuary, eastern China. *Chem. Geol.*, **202**, 383-396, doi: 10.1016/j.chemgeo.2002.05.001. [[Link](#)]
- Wells, M. L., G. J. Smith, and K. W. Bruland, 2000: The distribution of colloidal and particulate bioactive metals in Narragansett Bay, RI. *Mar. Chem.*, **71**, 143-163, doi: 10.1016/S0304-4203(00)00046-3. [[Link](#)]
- Wen, L. S., M. C. Stordal, D. Tang, G. A. Gill, and P. H. Santschi, 1996: An ultraclean cross-flow ultrafiltration technique for the study of trace metal phase speciation in seawater. *Mar. Chem.*, **55**, 129-152, doi: 10.1016/S0304-4203(96)00052-7. [[Link](#)]
- Wen, L. S., P. H. Santschi, and D. Tang, 1997: Interactions be-

- tween radioactively labeled colloids and natural particles: Evidence for colloidal pumping. *Geochim. Cosmochim. Acta*, **61**, 2867-2878, doi: 10.1016/S0016-7037(97)00139-7. [[Link](#)]
- Wen, L. S., P. Santschi, G. Gill, and C. Paternostro, 1999: Estuarine trace metal distributions in Galveston Bay: Importance of colloidal forms in the speciation of the dissolved phase. *Mar. Chem.*, **63**, 185-212, doi: 10.1016/S0304-4203(98)00062-0.
- Wen, L. S., K. T. Jiann, and P. H. Santschi, 2006: Physico-chemical speciation of bioactive trace metals (Cd, Cu, Fe, Ni) in the oligotrophic South China Sea. *Mar. Chem.*, **101**, 104-129, doi: 10.1016/j.marchem.2006.01.005. [[Link](#)]
- Zhang, J., 1995: Geochemistry of trace metals from Chinese River/Estuary systems: An overview. *Estuar. Coast. Shelf Sci.*, **41**, 631-658, doi: 10.1006/ecss.1995.0082. [[Link](#)]
- Zhang, J. and C. L. Liu, 2002: Riverine composition and estuarine geochemistry of particulate metals in China - weathering features, anthropogenic impact and chemical fluxes. *Estuar. Coast. Shelf Sci.*, **54**, 1051-1070, doi: 10.1006/ecss.2001.0879. [[Link](#)]