Antimony and arsenic biogeochemistry in the East China Sea

Jing-Ling Ren^{1,2}, Xu-Zhou Zhang^{1,2}, You-Xu Sun^{1,2}, Su-Mei Liu^{1,2}, Daji Huang^{3,4}, Jing Zhang⁵

¹ Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China;

² Qingdao Collaborative Innovation Center of Marine Science and Technology, Qingdao 266100, China;

³ State Key Laboratory of Satellite Ocean Environment Dynamics, Second Institute of Oceanography, State Oceanic Administration, Hangzhou 310012, China;

⁴ Ocean College, Zhejiang University, Hangzhou, 310058, China;

⁵ State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai 200062, China

* Corresponding author: Tel +86-532-66782005

Fax +86-532-66781810

E-mail renjingl@ouc.edu.cn

Abstract:

The biogeochemical cycles of the metalloid elements arsenic and antimony in the East China Sea (ECS), one of the most important marginal seas for western Pacific, were examined in May 2011. Dissolved inorganic arsenic (As(V) and As(III)) and antimony (Sb(V) and Sb(III)) species were determined by selective hydride generation–atomic fluorescence spectrometry (HG-AFS). Results show that total dissolved inorganic arsenic (TDIAs; $[TDIAs] = [As(V)] + [As(III)]$) were moderately depleted in the surface water and enriched in the deep water. Arsenite (As(III)) showed different vertical profiles with that of TDIAs, with significant surface enrichment in the middle shelf region where the concentrations of phosphate were extremely low. Speciation of dissolved arsenic was subtly controlled by the stoichiometric molar ratio of arsenate (As(V)) to phosphate. The average As(V)/P ratio for the ECS in spring 2011 was 10.8×10^{-3} , which is higher than previous results and indicates the arsenate stress. The concentrations of total dissolved inorganic antimony (TDISb; $[TDISb] = [Sb(V)] + [Sb(III)]$) were high near the Changjiang Estuary and the coastal area of Hangzhou Bay and decreased moderately off the coast. TDISb displayed moderate conservative behavior in the ECS that confirms by the correlations with salinity and dissolved aluminum. Different with that of As(III), antimonite (Sb(III)) concentrations were extremely lower in the ECS, with relative higher concentration appeared at the bottom layer which indicates the contribution from sediment-water interface. A preliminary box model was established to estimate the water-mass balance and antimony budgets for the ECS. Compared with other areas in the world, the concentrations of dissolved inorganic arsenic and antimony in the ECS remain at natural levels.

Keywords: arsenic; antimony; speciation; biogeochemistry; East China Sea

1. Introduction:

The East China Sea (ECS) is one of the largest marginal seas in the western Pacific Ocean, characterized by the seasonal variability of monsoons and interacting with large rivers (e.g. Changjiang) and Kuroshio in their western and eastern boundaries, respectively (Zhang and Su, 2004). The Changjiang (Yangtze River) contributes nearly 90% of the whole river discharges into the Yellow Sea and East China Sea (Zhang et al., 2007), with annual water and sediment discharges of about $928.2 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ and $0.49 \times 10^9 \text{ tons yr}^{-1}$ (decreased to $0.154 \times 10^9 \text{ tons yr}^{-1}$ at Datong gauging station during 2003-2008 due to the impoundment of Three Gorges Dam at Yichang (Milliman and Meade, 1983; Li et al., 2011; Wang et al., 2011)), of which ~70% is in the wet season (May-October) (Chen et al., 2008). The Changjiang Diluted Water (CDW) extends northeastward to the vicinity of Cheju Island in summer, while hugs the Chinese coast southwestward within a narrow band in winter (Chang and Isobe, 2003). The main currents flowing into and out of the ECS are the Kuroshio Current (KUC) flowing along the shelf break, the Taiwan Strait Warm Water (TSWW) entering through the Taiwan Strait, and the Tsushima Current (TSC) exiting through the Tsushima Strait (Su and Pan, 1987; Teague et al., 2005; Guo et al., 2006).

As members of Group 5 in the Periodic Table of Chemical Elements, trace elements arsenic (As) and antimony (Sb) might have similar chemical properties with that of phosphate. Both As and Sb occur in several oxidation states (+5, +3, 0, -3), in which the pentavalent arsenate (AsO_4^{3-}) and antimonate (SbO_4^{3-}) are the predominantly forms existed in most oxygenated surface waters. The biogeochemical cycling of As and Sb is complicated by the existence of multiple chemical species, diverse sources, selective uptake and different toxicities (Andreae, 1979; Cutter and Cutter, 1995).

1 The sources of metalloid elements in the natural waters are from riverine input, from upwelling of
2 subsurface waters and also from atmospheric deposition. Anthropogenic emissions of Sb and As to
3 the atmosphere have exceeded the natural sources ([Cutter and Cutter, 1995](#); [Nriagu, 1989](#)). The
4 enrichment factors (relative to the element/Sc ratios of typical crust rocks) for Sb and As are 70
5 and 20, respectively ([Shotyk et al., 1996](#); [Filella et al., 2002](#)).

6 Most studies of As biogeochemistry in the ocean have demonstrated that dissolved As shows
7 nutrient-like profile like phosphate (minor surface depletion and deep-water enrichment), with
8 concentrations ranging from 14 to 25 nM ([Andreae, 1979](#); [Middelburg et al., 1998](#); [Cutter and](#)
9 [Cutter, 1998](#); [Cutter et al., 2001](#); [Cutter and Cutter, 2006](#)). Despite the thermodynamic instability
10 in the presence of oxygen, arsenite (As(III)) is also found in natural waters at the nanomolar level,
11 which is believed to be due to the presence of a reducing environment, biologically mediated by
12 phytoplankton production, bacterial dissimilatory reduction, or photochemical generation ([Neff,](#)
13 [1997](#); [Oremland et al., 2000](#); [Oremland and Stolz, 2003](#)). Recently, arsenite has been suggested as
14 a chemical proxy of phosphate limitation in combination of alkaline phosphate activity (APA)
15 ([Wurl et al., 2013](#)). More and more results have shown that phytoplankton could uptake arsenate
16 and release arsenite or methyl arsenic as a function of phosphate concentration, due to the
17 similarity of chemical properties between arsenate and phosphate ([Sanders et al., 1994](#); [Cutter et](#)
18 [al., 2001](#); [Hellweger et al., 2003](#); [Cutter and Cutter, 2006](#); [Ren et al., 2010](#)). Additionally,
19 methylated arsenicals (e.g., monomethylarsenic (MMA), dimethylarsenic (DMA)) can be
20 produced through phytoplankton detoxification, microbial action, or bioaccumulation and release,
21 which are dominant over other organoarsenicals ([Andreae and Klumpp, 1979](#); [Sanders and Riedel,](#)
22 [1993](#); [Millward et al., 1996](#)). Organic species of As are usually found as minor fractions of total

1 As in natural waters ([Andreae, 1979; Cutter et al., 2001](#)).

2 The oceanographic distributions of dissolved Sb have far less been reported compared to As.

3 The oceanic behavior of Sb is quite different with that of As, showing either conservative behavior

4 or mildly scavenged vertical profile in the open ocean ([Middelburg et al., 1998; Cutter and Cutter,](#)

5 [1995, 1998; Cutter et al., 2001](#)). Antimonite (Sb(III)) and methylated antimony (primarily

6 monomethyl (MMSb)) are also detected in surface waters ([Ellwood and Maher, 2002](#)). However,

7 there are no results to support that Sb show a similar detoxification pathway like As. The sources

8 of reduced and methylated Sb are still remained unidentified.

9 China holds large reserves of As and Sb ores and is also one of large producing countries in the

10 world ([Carlin, 2000; Xiao et al., 2008](#)). China produced 1.5×10^5 tons yr^{-1} of Sb in 2012, which

11 contributed more than 80% of world mine production ([Carlin, 2000; Filella et al., 2002; Wang et](#)

12 [al., 2014](#)). The drainage basin of the Changjiang has abundant mineral resources of As and Sb. The

13 concentrations of Sb in rivers around the world's largest Sb mine of Xikuangsha (Hunan Province,

14 China) ranged from 6 $\mu\text{g/l}$ to 6384 $\mu\text{g/l}$ for waters and from 57 mg/kg to 7316 mg/kg for

15 sediments, which revealed the serious contamination compared to the average Sb concentrations in

16 world rivers (1 $\mu\text{g/l}$) and soils (1 mg/kg) ([He and Wan, 2004; Wang et al., 2011](#)). The impact of

17 anthropogenic activities (e.g. mining and agricultural use (herbicides, pesticides, and fungicides))

18 on the ECS and the north western Pacific Ocean are needed to be investigated. For our knowledge,

19 there are some results of dissolved arsenic in the major rivers and marginal seas of China ([Huang](#)

20 [et al., 1998; Yao et al., 2006, 2007; Duan et al., 2010; Ren et al., 2010; Li et al., 2014](#)). However,

21 there are few works about the biogeochemical behavior of antimony in the ECS ([Zhang et al.,](#)

22 [2014](#)). The present study examines the distribution of As (III), TDIAs, Sb (III) and TDISb in the

ECS in spring of 2011, attempts to elucidate the influence of chemical, hydrographic and biochemical processes on their distribution, and to understand the As and Sb dynamics with sustainability of ecosystems.

2. Materials and Methods

2.1 Station locations and sampling

The field observation was carried out in the southern part of Yellow Sea (YS) and ECS aboard the *R/V “Shi Yan 3”* between May 11 and June 7 of 2011 (Fig. 1). Sampling stations were mainly located in the ECS and only few stations were located in the southern YS to cover the buoyant plume from the Changjiang, only the ECS is provided for the name of study area in the following text. The observations were carried out from the southernmost section T (St. T3) to the northernmost section M (St. M7) from May 14 through May 27, except for the stations B1, B0, C1 and C0 located near the Changjiang Estuary, which were observed on June 2 due to the influence of typhoon “Sangda”. Two representative sections, PN section (a southeast transect from the Changjiang Estuary to the Ryukyu Islands) and KWL section (northeastward section along the shelf edge of the ECS from northeast of Taiwan to PN section), were chosen to discuss the impact of the Changjiang on the shelf region and material exchange between Kuroshio and shelf waters, respectively.

A CTD-rosette assembly with Niskin bottles (Model Sea-Bird 911plus) was used to measure the profiles of temperature, salinity, turbidity, and epifluorescence in the water column at grid stations. Discrete water samples were taken for nutrients, arsenic and antimony at depths determined from CTD readings. After collection, samples were filtered through precleaned 0.4- μm pore-size Nuclepore polycarbonate filters (Whatman Co., soaked in HCl solution (pH 2) for a whole day and

1 in Milli-Q water (purified with a water purification system, Millipore, USA) until a neutral pH
2 was reached) in a Class-100 clean bench. Suspended particulate matter (SPM) was measured by
3 weighing the particles trapped on the filters. The filtrates were kept in Nalgene LDPE bottles and
4 frozen at -20 °C until measurement. Blanks were carefully prepared by filtering on board a known
5 volume of Milli-Q water with methods identical to those used on the bulk sample sets.

6 2.2 Analytical Methods

7 Dissolved arsenite and total dissolved inorganic arsenic (TDIAs, $[TDIAs]=[As(V)]+[As(III)]$)
8 were measured using hydride generation–atomic fluorescence spectrometry (HG-AFS). Arsenite
9 concentrations were determined at pH 5.3–5.5 buffered by sodium citrate–HCl solution, in which
10 arsenate was not allowed to be reduced to arsenite. Arsine (AsH_3) generation by the reduction of
11 potassium borohydride (KBH_4 , 0.7%) with flow rate of 0.6–0.7 ml/s was thus limited to the As(III)
12 initially present in the sample. AsH_3 was carried out of solution by argon gas with flow rate of 800
13 ml/min and measured by AFS. TDIAs was determined with the same method with As (III) except
14 for the acidity of 1 M HCl, after reducing arsenate into arsenite by thiourea (5%)–Vc (3%) mixed
15 solution for 90 min (Li, 2003). The concentration of arsenate was calculated from the difference of
16 TDIAs and As(III), assuming arsenic species other than arsenate and arsenite were negligible in
17 quantity. The detection limits for TDIAs and As(III) by HG-AFS were 0.11 and 0.02 nM,
18 respectively. The precision of HG-AFS measurement for TDIAs was 6.8% at the concentration of
19 1.6 nM and for As(III) was 3.1% at the concentration of 1.3 nM. To test the robustness of the
20 present method, the national reference standard sample (GSBZ50004-883610116, Institute for
21 Environmental Reference Materials of Ministry of Environmental Protection) and international
22 standard reference sample (NASS-4) were analyzed. The certified value of As in

1 GSBZ50004-883610116 is $1.72 \pm 0.10 \mu\text{g L}^{-1}$, and the result from our method was $1.73 \pm 0.01 \mu\text{g}$
2 L^{-1} (n=7). The certified value of As in NASS-4 is $1.26 \pm 0.09 \mu\text{g L}^{-1}$, and the result from our
3 method was $1.28 \pm 0.04 \mu\text{g L}^{-1}$. The difference between our method and the certified value was
4 within 2%, which ensures the quality of our HG-AFS method (Ren et al., 2010).

5 Dissolved antimonite (Sb(III)) and total dissolved inorganic antimony (TDISb,
6 $[\text{TDISb}] = [\text{Sb(V)}] + [\text{Sb(III)}]$) were measured using hydride generation–atomic fluorescence
7 spectrometry (HG-AFS). Sb (III) concentrations were determined at pH 4.0–4.5 buffered by
8 sodium citrate–HCl solution, in which antimonate was not allowed to be reduced to antimonite.
9 Antimony hydride (SbH_3) generation by the reduction of KBH_4 (0.5%) with flow rate of 0.6–0.7
10 ml/s was thus limited to the Sb (III) initially present in the sample. SbH_3 was carried out of
11 solution by argon gas with flow rate of 600 ml/min and measured by AFS. TDISb were
12 determined with the same method with Sb (III) except for the acidity of 1 M HCl, after reducing
13 antimonate into antimony hydride by thiourea (5%)–Vc (3%) mixed solution for 90 min (Wan and
14 Ren, 2011). The concentration of antimonate was calculated from the difference of TDISb and Sb
15 (III), assuming antimony species other than antimonate and antimonite were negligible in quantity.
16 The detection limit for TDISb and Sb (III) were 0.20 nM and 0.011 nM, respectively. The
17 precision of HG-AFS measurement for TDISb was 1.9 % at the concentration of 0.25 nM and for
18 Sb (III) was 5.5 % at the concentration of 0.08 nM. The precision and accuracy of inorganic Sb
19 analysis were monitored using national reference standard solution (GSB G 62043-90 (5101),
20 China National Center for Quality Supervision and Testing of Iron and Steel). The recoveries for
21 TDISb and Sb (III) are 93.7%~105% and 91.1%~104%, respectively.

22 3. Results

3.1 Hydrography

[Table 1](#) gives the ranges and average concentrations of temperature, salinity, SPM and different species of As and Sb. According to the horizontal distributions of temperature, salinity and suspended particulate matter (SPM) ([Fig. 2a-f](#)) and the relationships between temperature and salinity at sections PN and KWL ([Fig. 3](#)), five major water masses in the ECS during the expedition can be commonly differentiated. Changjiang Diluted Water (CDW) flows along the coast of mainland of China, which is characterized by high concentrations of nutrient and SPM and low salinity. Taiwan Strait Warm Water (TSWW) flows northward through the Taiwan Strait, which is characterized by low concentrations of nutrient and SPM and high temperature and salinity. Kuroshio intrudes onto the shelf region from the north of Taiwan and its main axis flows northward along the shelf edge of the studied area, which includes the warm, high salinity and nutrient-poor Kuroshio Surface Water (KSW) and the cold, high salinity and nutrient-rich Kuroshio Subsurface Water (KSSW) and Kuroshio Intermediate Water (KIW).

The water column was well-mixed in the shallow regions and was generally stratified in the central ECS, with relatively lower temperature and higher salinity and SPM in the bottom layer. CDW expanded southeastward in the surface and was restricted by the incursion of Kuroshio Waters ([Figs. 3, 5](#)). Another low salinity water tongue existed near the coast of Zhejiang and Fujian Provinces (here in after Zhe-Min coast) in the surface, which indicated riverine inputs (e.g. Oujiang) in the Zhejiang Province. A fairly strong vertical gradient for salinity and temperature, characteristic of the Kuroshio waters (KW), occurred at the Okinawa Trough. Kuroshio Waters occupied in the middle shelf region and shelf edge, especially in the bottom layer where the incursion of KSSW can reach 30 °N near the Changjiang Estuary. The concentration of SPM

1 decreased rapidly off the river mouth and showed uniform concentrations of 2–5 mg L⁻¹ in the
2 shelf area. An increase in SPM concentration was observed in the bottom waters owing to
3 resuspension.

4 3.2 Arsenic species in the East China Sea

5 3.2.1 Horizontal distribution

6 The ranges and average concentrations for arsenic species in the surface and bottom layers of
7 the ECS in the spring of 2011 are summarized in [Table 1](#). TDIA concentrations varied from 8.7 to
8 24.1 nM in the ECS, with an average of 16.2 nM. TDIA concentrations were high in the coastal
9 area of the Changjiang Estuary and Hangzhou Bay and decreased rapidly off the coast in the
10 surface, which indicated the effect of land-source input from the adjacent rivers ([Fig. 4a-b](#)). There
11 existed mild surface depletion of TDIA concentrations at the northern and eastern part of the
12 study area. The concentration of TDIA at the surface of St. D9 (located in the Okinawa trough)
13 was 3.5–4.5 nM higher than the neighboring Sts. ED and DC. Horizontal distribution of TDIA in
14 the near bottom layer was similar to that in the surface, with relatively higher concentrations. High
15 concentrations of TDIA could also be seen at the near bottom of northeast of Taiwan and eastern
16 of the study area, with low SPM contents.

17 Arsenite concentrations ranged from 0.15 to 8.52 nM in the ECS, with an average of 0.92 nM.
18 Arsenite showed different horizontal distribution features from TDIA, with higher concentrations
19 in the surface water of the upwelling region at the south of the Changjiang Estuary and the middle
20 and eastern shelf area, corresponding to the area with surface depletion of TDIA ([Fig. 4c-d](#)). The
21 concentrations of As (III) in the bottom layer were significantly lower than the surface, especially
22 at the region affected by the incursion of KSSW. The ratio of As(III)/TDIA ranged from 0.01 to

1 0.56, with an average of 0.06.

2 3.2.2 Vertical distribution

3 Sections PN (C0-CJ) and KWL (G8-CJ) with water depth >200 m and off the shelf, were chose
4 to discuss the vertical distributions of As and the impacts of terrestrial input on the ECS shelf and
5 material exchange between shelf water and Kuroshio Waters (Figs. 5-6). They were also used to
6 examine the escape of terrestrial materials across the broad shelf and the impact of Kuroshio from
7 open ocean.

8 In section PN, the water column was vertically well mixed in the coastal area of the Changjiang
9 Estuary, with the characteristic of low temperature and low salinity indicating the existence of
10 CDW, showing the influences of terrestrial waters on the shelf up to a distance of ~280 km at
11 Stations C5 and C7. The water column was weakly stratified in the central and eastern ECS, with
12 warm and less saline water mass in the surface and cold and saline water mass in the bottom,
13 indicating the impact of Kuroshio from the shelf edge (St. CJ) into the middle shelf region
14 (between Sts. C4 and C2). The concentrations of SPM were high and well mixed in the coastal
15 area of the Changjiang Estuary and decreased quickly offshore (Fig. 5a-c), with relatively lower
16 concentration in the outer shelf and shelf edge. TDIAs concentrations were high and vertically
17 homogeneous near the Changjiang Estuary, with slight segregation in the shelf region (Fig. 5d).
18 TDIAs showed mild surface depletion and deep-water enrichment in the mid shelf and shelf break.
19 A water mass with relatively high concentration of TDIAs occupied the bottom layer of water
20 column at the shelf edge and intruded onto the shelf region. Arsenite showed different vertical
21 profile with that of TDIAs, with relatively high concentration appearing at the surface of mid shelf
22 and decreasing with depth (Fig. 5e).

1 The Kuroshio forms as a northward branch of the westward North Equatorial Current at east of
2 Luzon Island and flows northward, with a volume transport of ca. 23-37 Sv ([Hsin et al., 2008 and](#)
3 [references therein](#)). Section KWL, originating from the north of Taiwan to the end of PN section
4 along the Okinawa Trough, is set to discuss the possible material exchange between shelf water
5 and Kuroshio water. In KWL section, the water column was stratified with decreasing temperature
6 and increasing density with depth ([Fig. 6a-c](#)). There existed a water tongue with relatively higher
7 salinity (ca. 34.7) in the water depth of 50-150 m of all sampling stations, which indicated the
8 incursion of KSSW, seen in previous observations ([Ren et al., 2006](#)). SPM concentrations were
9 low in the whole section, except for slight increasing at the top 100 m water layer of St. CJ ([Fig.](#)
10 [6d](#)). TDIAs concentrations were depleted in the surface and increased with depth generally,
11 showing the character of the open ocean ([Middelburg et al., 1988; Cutter et al., 2001; Cutter and](#)
12 [Cutter, 2006](#)). As (III) concentrations in the top 100 m water column between St. G8 and St. D9
13 were 8 folds lower than that in the PN section, and increased slightly towards the end of PN
14 section (e.g. Sts. DC and CJ). As (III) concentrations in the deep water were similar with that in
15 the PN section and showed the characteristics of deep open ocean ([Fig. 6e](#)).

16 3.3 Antimony species in the East China Sea

17 3.3.1 Horizontal distribution

18 TDisb concentrations varied from 0.71 to 4.98 nM in the ECS, with an average of 1.84 nM.
19 Similar with the horizontal distributions of TDIAs, TDisb concentrations were high in the coastal
20 area of the Changjiang Estuary and Hangzhou Bay and decreased rapidly off the coast both in the
21 surface and bottom layers. Different with that of TDIAs, TDisb didn't show surface depletion and
22 bottom enrichment. The concentrations of TDisb only moderately increased in the bottom layer of

shelf break (~2 nM), which is different with that of TDIAs.

Antimonite concentrations ranged from BDL (below detection limit) to 0.30 nM in the ECS, with an average of 0.08 nM. Sb (III) showed patchy distributions both in surface and bottom layer, with relatively higher concentrations in the coastal area of the Changjiang Estuary and extremely lower concentrations in the middle shelf region in the surface. The concentrations of Sb (III) in the bottom layer were higher than the surface (Fig. 4g-h).

3.3.2 Vertical distribution

In section PN, TDISb concentrations were high and vertically homogenous near the Changjiang Estuary and decreased off the coast in the surface. In the bottom layer of middle shelf and shelf edge where is affected by the incursion of Kuroshio Waters, TDISb concentrations remained as less variable concentrations (e.g., 1.5 nM) as the deep water of the northwestern Pacific (Fig. 5f) (Cutter and Cutter, 2006). Sb (III) were only detectable at several layers at each stations and the figure is neglected here and after.

In KWL section, TDISb concentrations were high at St. G8 (locates at the northeast of Taiwan), especially at the mid and near-bottom layer, and decreased rapidly northeastward along the flow path of Kuroshio in the Okinawa Trough (Fig. 6f). Interestingly, the concentrations of TDISb at the subsurface layer of St. D9 are significantly higher than the neighbored stations ED and DC (2.2 nM compared to 1.7 nM in the neighboring stations with an increase of ca. 30%), which will be discussed later.

4. Discussion

4.1 Arsenic and Antimony regimes in the East China Sea

4.1.1 Arsenic regime

1 Average concentration of TDIAs in the ECS in May 2011 is 16.2 ± 2.5 nM, which is similar with
2 the result of September 2002 (15.6 ± 0.6 nM) and slightly higher than the result of September 2003
3 (14.2 ± 1.0 nM) (Ren et al., 2010). Average concentration of As (III) in the ECS shelf in May 2011
4 is 0.92 ± 1.13 nM, which is higher than the result of September of 2002 (0.65 ± 0.23 nM) and similar
5 with the result of September 2003 (1.04 ± 0.56 nM) (Ren et al., 2010). One thing should be kept in
6 mind is that the station locations between different cruises mentioned above are different, with
7 only independent sections observed in the autumn cruises (September 2002: section PN; section A,
8 from the Changjiang Estuary to Cheju Island; section B, from the Changjiang Estuary southwards
9 to Zhe-Min coast along the Chinese coast. September 2003: section PN; section YT, from the
10 Changjiang Estuary to St. S1 (129.15°E , 32.00°N); section AS, from St. S1 southwards to the end
11 of section PN (St. P3, 127.30°E , 28.44°N) and nearly uniformly covered from the north of the
12 Changjiang Estuary southwards to the Taiwan Strait in May 2011 cruise.

13 TDIA concentrations are high near the coastal area of the Changjiang Estuary and Hangzhou
14 Bay and at the bottom layer where Kuroshio Waters incursion onto the shelf. The concentration of
15 TDIAs at Xuliujing (located at the inner Changjiang Estuary with salinity ~ 0) was 38.1 nM based
16 on the field observation carried out at the early autumn of 2009 (unpublished data). Changjiang
17 brings TDIAs along with huge amounts of fresh water and sediment into the ECS, which is
18 believed to be the major source of TDIAs in the coasts and shallow water areas. A water tongue
19 with high TDIAs (17.9 ± 2.3 nM), high salinity and extremely low SPM concentrations at the
20 bottom of middle shelf and shelf edge suggests that the Kuroshio Waters are the other source of
21 TDIAs in the east. The concentration of TDIAs near the Taiwan Strait was about 15.9 ± 1.0 nM,
22 which can be used as the background value for the TSWW. The freshwater discharges (e.g., from

the Changjiang and other rivers in Fujian and Zhejiang provinces) mainly affected the coastal area and the surface of the shelf region, whereas the incursion of Kuroshio Waters can be tracked in middle and near bottom layer of the ECS.

Arsenite concentrations were lower than arsenate, with As (III)/TDIAs ratios ranging from 0.01 to 0.56 and with an average of 0.06 ± 0.08 , which indicates that arsenate is the main arsenic species in the study area. In comparison with TDIAs, As (III) showed different horizontal and vertical profiles. High arsenite concentrations were found at the surface near the Changjiang Estuary and at the surface of mid-shelf, corresponding to the area with significant surface depletion of TDIAs, which indicate different source of As (III) in the ECS shelf compared to TDIAs.

4.1.2 Antimony regime

Average concentrations of TDISb and Sb (III) in the ECS in May 2011 are 1.84 ± 0.66 and 0.08 ± 0.07 nM, respectively. Concentrations of TDISb and Sb (III) are slightly higher or comparable with other coastal regions and open oceans in the world (Table 2), including North and South Pacific (Ellwood and Maher, 2002; Cutter and Cutter, 2006), western and eastern Atlantic Ocean (Cutter and Cutter, 1995, 1998; Middelburg et al., 1988; Cutter et al., 2001), Amazon river and its plume (Cutter et al., 2001), which indicate that the concentration of TDISb in the ECS still remained at natural levels. The concentrations of TDISb in the lower reach of the Changjiang was 10.14 nM, while they ranged from 1.39 to 6.64 nM for the other rivers located in Zhejiang and Fujian provinces (Zhang et al., 2014). However, Sb (III) was not detectable in most stations located in the lower reaches of the Changjiang (unpublished data). Riverine discharge (e.g. Changjiang and other rivers in Zhejiang and Fujian provinces) is believed to be the major source of TDISb in the coasts and shallow water areas. Kuroshio Waters have relatively lower

concentrations of TDISb and Sb (III), which are not major source for Sb and is different with that of TDIAAs.

Sb (III) concentrations were lower than Sb (V), with Sb (III)/TDISb ratios ranging from BDL to 0.21 and with average of 0.05 ± 0.05 , which indicates that antimonate is the main antimony specie in the study area. In comparison with As (III), Sb (III) didn't show surface enrichment in the coastal area and mid-shelf region, suggesting different producing mechanisms with that of As (III). Sb (III) concentrations were higher in the near bottom layer relative to surface indicate the contributions from sediment-water fluxes.

4.2 Biogeochemical cycling of arsenic in the East China Sea

Previous studies of arsenic biogeochemistry carried out in the Pacific ([Andreae, 1979](#); [Ellwood and Maher, 2002](#); [Cutter and Cutter, 2006](#)), Atlantic ([Cutter and Cutter, 1995, 1998](#); [Middelburg et al., 1988](#); [Cutter et al., 2001](#)), Southern Ocean ([Santosa et al., 1994](#); [Featherstone et al., 2001](#)), Oslofjord of Norway ([Abdulliah et al., 1995](#)), continental shelf off the Gironde Estuary ([Michel et al., 1997](#)), Bohai Sea ([Duan et al., 2010](#)) and ECS shelf ([Ren et al., 2010](#)) have clearly shown linkages with phosphate cycling. The horizontal data observed in the western Atlantic Ocean suggested that arsenate uptake and the production of arsenite would increase when phosphate levels drop below ca. $0.05 \mu\text{M}$ ([Cutter et al., 2001](#)).

Surface depletion of arsenate and surface maximum of arsenite in the ECS in spring of 2011 ([Figs. 4-6](#)) suggests biota mediation of arsenic as revealed in the open oceans, although marginal sea receives huge amounts of nutrients from riverine discharges and incursion of Kuroshio ([Middelburg et al., 1988](#); [Michel et al., 1997](#); [Cutter and Cutter, 2001, 2006](#)). Strong phytoplankton blooms occurred intermittent from April 17 through April 27 2011 in the coastal

1 and northern ECS shelf according to the chlorophyll–sensing satellite images from NASA
 2 (http://oceancolor.gsfc.nasa.gov/cgi/13?ctg=Standard&sen=A&prd=CHL_chlor_a&per=DAY&date=1May2009&res=4km&num=24), with maximum chlorophyll a concentration higher than 10
 3 mg/m^3 . Figure 7 gives the vertical profiles of TDIAAs, As (III) and phosphate at stations C4 and C7.
 4 Water columns were slightly stratified at stations C4 and C7, with warm and less saline water at
 5 top mixed layer and cold and saline water below, indicating the effects from CDW and incursion
 6 of Kuroshio waters. TDIAAs showed minor surface depletion and deep water enrichment like
 7 phosphate in both stations, with correlation coefficients (r) of 0.94 and 0.83, respectively.
 8 Figure 8 gives the correlation between As (III)/TDIAAs ratio and phosphate concentrations. In
 9 general, As(III)/TDIAAs ratio keeps at extremely low value when phosphate concentrations are
 10 higher than 1.00 μM . However, As(III)/TDIAAs ratios start to increase exponentially with the
 11 decreasing of phosphate concentrations, especially when the concentrations of phosphate are
 12 lower than 0.25 μM . This relationship between As(III)/TDIAAs ratio and phosphate concentrations
 13 indicate the role of phosphate in arsenate depletion and the production of arsenite, which is similar
 14 with previous results in other open oceans. In order to differentiate the functions of biological
 15 mediation and phosphate depletion on the arsenic speciation transformation clearly, we separate
 16 the study area into three regions according to the geographical locations and the strength of
 17 biological activity, which is coastal area (within 50 m isobath), northern shelf (north of 28 °N with
 18 water depth deeper than 50 m) and southern shelf (south of 28 °N with water depth deeper than 50
 19 m) (Fig. 8). According to the chlorophyll–sensing satellite images from NASA, the bloom mainly
 20 occurred at the coastal area and the region north of 28 °N, which is corresponding to the area with
 21 significant As (III) surface enrichment (Fig. 4c). As(III)/TDIAAs ratios remain at relatively lower
 22

values in the southern ECS with weak phytoplankton activity. However, As(III)/TDIAs ratios increase dramatically with the decreasing of phosphate concentrations in the coastal and northern ECS where phytoplankton activities were high.

Plots of As (V) against phosphate levels show good correlations in the stations with significant TDIAs depletion in May 2011, with the stoichiometric molar ratios of As(V):P ranging from 1.2×10^{-3} to 20.9×10^{-3} and an average of 10.8×10^{-3} . The stoichiometric molar ratios of As(V):P are relatively high in the inner and middle shelf and lower at the shelf edge. Previous observations carried out in the PN section of ECS shelf in autumn 2002 and 2003 gave the molar ratios of 2.42×10^{-3} and 2.06×10^{-3} , respectively (Ren et al., 2010). In order to compared the results of the ECS between different seasons and years conveniently, the stoichiometric molar ratios of As(V):P at PN section in May 2011 are calculated, with average of 12.3×10^{-3} . These values in May 2011 are significantly higher than the results of autumn 2002 and 2003, indicate higher arsenate stress appeared in May 2011 compared to September 2002 and 2003 in the ECS shelf. The results are higher than North and South Atlantic Ocean (2.5×10^{-3} , Cutter and Cutter, 1995), western Atlantic Ocean ($(2.63 \pm 0.4) \times 10^{-3}$, Cutter et al., 2001) and fjords of Norway (2.54×10^{-3} to 3.16×10^{-3} , Abdullah et al., 1995), while similar with the 10×10^{-3} in the North Pacific where Andreae (1979) found evidence of arsenate stress.

4.3 Biogeochemical cycling of antimony in the East China Sea

Most previous studies of antimony from Atlantic Ocean, Pacific Ocean and adjacent seas showed either conservative or mildly scavenged behavior like aluminum and also showed the importance of atmospheric deposition on both vertical and horizontal distributions (Andreae and Froelich, 1984; Middelburg et al., 1988; Van der Weijden et al., 1990; Guieu et al., 1993; Cutter and

1 Cutter, 1995; Cutter et al., 2001; Cutter and Cutter, 2006). A confounding issue should be kept in
2 mind is that anthropogenic emissions will increase the concentration of Sb in atmospheric
3 deposition. Cutter and Cutter (2006) found that there existed linear correlation between the
4 concentrations of Al and Sb at station ALOHA (22.75°N, 158.0°W; farthest away from potential
5 anthropogenic inputs) with atomic Sb/Al ratio of 0.09. However, the correlations between TDISb
6 and Al decreased for the stations located at the western North Pacific where received more
7 anthropogenic Sb relative to Al (Cutter and Cutter, 2006).

8 TDISb negatively correlates with salinity (with salinity range of 23.40 and 34.90), with fitting
9 equation of $y = -0.2528x + 10.18$ and linear relationship coefficient of 0.75 (n=310, figure is not
10 shown), which is similar with the previous result of the coastal area of Zhe-Min coast (Zhang et al.,
11 2014) and indicates that physical mixing of different water masses is the major influencing factor
12 of the biogeochemical behavior of TDISb. There are no apparent correlations between TDISb and
13 SPM, DO and phosphate (figures are not shown) in the ECS in May 2011, neither for Sb(III)/Sb(V)
14 ratio. There exists linear correlation between the concentrations of dissolved Al (unpublished data)
15 and TDISb in the ECS in May 2011 ($r=0.43$, n=310) with atomic Sb/Al ratio of 0.011, which is
16 lower than the results from station ALOHA (Cutter and Cutter, 2006). The relatively lower atomic
17 Sb/Al ratio compared to station ALOHA is mainly due to higher concentration of dissolved Al
18 compared to Sb in the marginal seas.

19 Figure 9 gives the vertical profiles of TDISb at stations G8, ED, D9 and DC, which locate at the
20 section KWL where affected by the incursion of Kuroshio from south to north. In order to
21 compare the vertical profiles of TDISb in the ECS with the open ocean, TDISb results from station
22 1 (34.467°N, 146.99°E, locates at the northern edge of the subtropical gyre in the Kuroshio

1 Current, western North Pacific, [Cutter and Cutter, 2006](#)) are redraw and included in [Figure 9](#).
2 Compared to St. 1 in the western North Pacific, TDISb concentrations at St. G8 are significantly
3 higher in the subsurface layer (50-200 m) and middle layer (400-800 m). Salinities of water
4 column of St. G8 with layer at σ_T value 23.63 and 24.06 (corresponding to the water depth of
5 nearly 95-120 m) and 24.51 and 25.00 (corresponding to the water depth of nearly 175-205 m) are
6 significantly lower than the other stations in section KWL within similar isopycnal intervals.
7 However, salinities of seawater with σ_T value larger than 26.31 (corresponding to the water depth
8 of 400-1000 m) are significantly higher than the other stations ([Fig. 3](#)). The difference between St.
9 G8 and other stations in T-S diagram of section KWL ([Fig. 3](#)) might indicate the contributions
10 from the South China Sea (SCS) ([Chen, 2005](#)). South China Sea Tropical Water (SCSTW) and
11 South China Sea Intermediate Water (SCSIW), outflowing modified Kuroshio waters from the
12 SCS through Luzon Strait and with the characteristic of salinity maximum within the water depth
13 of 50-150 m and comparatively higher salinity minimum within the water depth of 350 and 1350
14 m deep, contains more nutrients than does the Kuroshio Waters due to the strong upwelling in the
15 SCS basin ([Nitani, 1972](#); [Chen and Wang, 1998](#); [Chen, 2005](#)). The existence of the impacts from
16 SCSTW and SCSIW might explain the relative higher concentrations of TDISb at subsurface layer
17 and 400-800 m layer due to the contributions from the SCS.

18 Along with the northward movement of Kuroshio, the concentrations of TDISb are decreased
19 by the sequence of St. ED and St. DC (except for St. D9) and closed to the value of Station 1 due
20 to the dilution of Kuroshio. Vertical profile of TDISb at station DC, the deepest station in section
21 KWL (1588 m, bottom sample was not collected due to the technical problems) which means
22 receiving lest impact from continental shelf, is nearly coincide with the profile of St.1 except for

the surface enrichment. Surface enrichment of TDISb at station DC compared to St. 1 is mainly due to the reception of terrestrial material from riverine and atmospheric deposition and represents the characteristics of marginal seas.

Vertical profile of TDISb at St. D9 doesn't follow the general variation along with the northward movement of Kuroshio and shows abnormally higher concentrations at top 200 m layer and similar profile with St. DC at the water column deeper than 200 m (1.94 nM compared to 1.47 nM with an increase of ca. 30%). Atmospheric deposition solely can't explain the enrichment of TDISb within top 200 m water column, and will be discussed later. The existence of cross shelf transport from ECS shelf to the Kuroshio can be the possible reason and we really found the evidence from the distributions of dissolved Al (unpublished data). The contribution of cross shelf transport from marginal seas to the open ocean needs to be paid more attention.

4.4 Antimony budgets in the East China Sea

Arsenic budgets in the summer for the ECS was evaluated before based on box models for the conservation of water and salt masses and are not re-evaluate in this manuscript (Ren et al., 2010). Antimony budgets in the ECS are evaluated and listed in Table 3, based on the water budgets in the summer summarized by Zhang et al. (2007) and simplified one-box model described by Gordon et al. (1996). The major potential sources of antimony into the ECS include river runoff (mainly from Changjiang discharge which accounts for ca. 90–95% of total riverine discharges and neglect the contributions from other rivers); the intrusion of oceanic water from the Kuroshio (from north of Taiwan, mainly composed of the KSW (i.e., 25%) and the KSSW (i.e., 75%)); the water flux through the Taiwan Strait (TSWW) and atmospheric deposition (both dry and wet deposition). The outflow of antimony is mainly accompanied by the water exchange between the

1 Yellow Sea and the ECS and with currents through the Tsushima/Korea Strait. The contributions
2 from submarine groundwater discharge (SGD) and sediment water interface are ignored in [Table 3](#)
3 due to lack of relevant data.

4 The range and average concentration of TDISb for the Changjiang are from our ongoing
5 monitoring station (Xuliujing, i.e. 160 km inland from the river mouth with salinity of ~0), which
6 was monitored every month from July 2012 to June 2013, with average of 11.4 nM (unpublished
7 data). The influx from other rivers was not included owing to their minor contribution. The mean
8 concentrations of TDISb in the top 50 m and a depth interval of 50-200 m at stations located at the
9 section of KWL were taken as the KSW and KSSW ([Nitani, 1972](#); [Wong et al., 2000](#)). The
10 average concentration of TDISb at stations T1 and T3 are used as the end-member of TDISb for
11 the inflow from the Taiwan Strait (TSWW).

12 Recent results from peat bogs and ice cores have demonstrated that anthropogenic sources of Sb
13 have dominated the atmospheric inputs to the open ocean at least 700 years ([Krachler et al., 2008](#)
14 [and references therein](#)). The atmospheric deposition flux of Sb should be included in budgetary
15 work considering the reasons that China is an important producing country of Sb products in the
16 world and significant annual aerosol transport from mainland Asia to the North Pacific ($\sim 480 \times$
17 $10^{12} \text{ g yr}^{-1}$, [Duce et al., 1991](#)). The atmospheric Sb concentrations in the ECS based on the aerosol
18 samples collected during cruises between the spring of 2005 and the spring of 2007 were 2.8 ng
19 m^{-3} (n=7), 1.1 ng m^{-3} (n=33) and 0.8 ng m^{-3} (n=7) for winter, spring and summer, respectively
20 ([Hsu et al., 2010](#)). There were no aerosol samples collected in autumn. The average atmospheric
21 Sb concentration in the ECS is $1.57 \pm 1.08 \text{ ng m}^{-3}$ if we assume the concentration in autumn is
22 similar with that of summer. Mean dry deposition velocity for aerosol particles of Sb in the ECS

1 was $2.0 \pm 1.5 \text{ cm s}^{-1}$ based on mass particle-size distributions and other observation and model
2 calculation (Uematsu et al., 1985; Duce et al., 1991; Gao et al., 1997; Hsu et al., 2009). Then, the
3 dry deposition fluxes of Sb in ECS can be estimated by the formula of $F = V_d \times C_a$, in which V_d
4 represents the dry deposition velocity and C_a represents the atmospheric concentration of Sb, with
5 the result of $0.050 \pm 0.02 \text{ mol s}^{-1}$ considering the average solubility of Sb from aerosol samples as
6 $36 \pm 7\%$ (Hsu et al., 2010). Due to the absence of wet deposition data for Sb in the ECS, total
7 atmospheric deposition flux of Sb is estimated to be $0.18 \pm 0.09 \text{ mol s}^{-1}$ assuming that the
8 proportion of dry and wet deposition flux of Sb is similar with that of annual eolian dust fluxes
9 through dry (27%) and wet (73%) deposition (Hsu et al., 2009) and the solubility of Sb in the dry
10 and wet deposition is same. Total atmospheric input of Sb into the East China Sea is nearly half of
11 the input from the rivers, with obvious seasonal and sporadic characteristics. However, the
12 atmospheric deposition of Sb maybe underestimated due to the ignorance of significant
13 contributions from rainwater which can flush out trace elements from aerosol particles thoroughly
14 (Ren et al., 2011) and need to be studied in the near future.

15 The output and input are nearly same for antimony in the ECS based on the calculations in
16 Table 3, which are different with the mass balance results of arsenic (Ren et al., 2010). In case of
17 arsenic, the input is higher than output with a value of 9.9 mol s^{-1} which indicates the net sinks of
18 arsenic due to the species transformation and burial into the sediments. However, antimony is
19 quite conservative compared to arsenic, which is same with the discussion before.

20 5. Conclusions

21 The concentrations of dissolved arsenic and antimony in the ECS are comparable to the other
22 marginal area and open ocean, which demonstrate that the potential anthropogenic impacts from

1 the mainland of China are not significantly affect the background concentration. For dissolved
2 inorganic arsenic (III, V) and antimony (III, V) examined in the ECS, all display the effects from
3 riverine inputs, atmospheric deposition, intrusion of Kuroshio Waters and Taiwan Strait Warm
4 Waters. Pentavalent (arsenate and antimonite), the thermodynamically form, are the major
5 speciation in the ECS in spring for both arsenic and antimony. TDIAs shows moderate surface
6 depletion and bottom enrichment profiles like phosphate, with significant surface maximum of As
7 (III) in the region with lower concentration of phosphate. High As(V)/P atomic ratio have been
8 observed in spring of the ECS, which is four to five folds higher than the results of ECS shelf in
9 autumn 2002 and 2003 and indicates more arsenate stress in spring. In contrast, antimony showed
10 moderate scavenged and conservative profiles in the ECS, with less evidence of biological
11 mediation. The variations of horizontal and vertical profiles of Sb (V) are sensitive to the
12 atmospheric deposition and riverine inputs, which make it a good tracer for the transport of
13 terrestrial material. Vertical profiles of TDISb at KWL section, originating from northeast of
14 Taiwan and northeastward along with the current of Kuroshio, suggests the significant
15 contributions from SCSTW and SCSIW and indicates the possible position of cross shelf transport
16 from ECS to the Kuroshio. Box model calculation of antimony in the ECS demonstrates that the
17 major sources of Sb are riverine input, atmospheric deposition, the incursion of Kuroshio and
18 water flux through Taiwan Strait (TSWW), and the major sinks are through the outflow currents
19 through the Tsushima/Korea strait. The input and output fluxes of Sb are nearly balanced which
20 demonstrate the rationality of box model calculation.

21

22 **Acknowledgement**

1 This study was funded by National Basic Research Program of China (973 project,
 2 2011CB409801), National Science Foundation of China (41176096) and the Program of
 3 International S&T Cooperation (No. 2010DFA24590). The authors thank the captain and crew of
 4 *R/V “Shiyan 3”*, X.H. Cao and C.L. Xin for their assistance in the field and laboratory work, Z.W.
 5 Wang for his assistance of figure preparation. Drs. J. Li and R.F. Zhang are acknowledged for their
 6 help of hydrographic data managements during the execution of 973 project.

7

8 **References**

- 9 Abdullah, M. I., Zhou, S. Y., Kare, M., 1995. Arsenic and selenium species in the oxic and anoxic
 10 waters of the Oslofjord, Norway. *Mar. Pollut. Bull.* 31, 116-126.
- 11 Andreae, M. O., Froelich, P. N., 1984. Arsenic, antimony, and germanium biogeochemistry in the
 12 Baltic Sea. *Tellus Ser. B* 36, 101–117.
- 13 Andreae, M.O., 1979. Arsenic speciation in seawater and interstitial waters: the influence of biological
 14 – chemical interactions on the chemistry of a trace element. *Limnol. Oceanogr.* 24, 440 – 452.
- 15 Andreae, M.O., Klumpp, D., 1979. Biosynthesis and release of organo-arsenic compounds by marine
 16 algae. *Environ. Sci. and Technol.* 13, 738-741.
- 17 Carlin Jr., J.F., 2000. Antimony. U.S. Geological Survey Mineral Commodity Summaries.
- 18 Chang, P.H., Isobe, A., 2003. A numerical study on the Changjiang diluted water in the Yellow and East
 19 China Seas. *J. Geophys. Res.* 108, C9, 3299, doi:10.1029/2002JC001749.
- 20 Chen, C.-T. A., 2005. Tracing tropical and intermediate waters from the South China Sea to the
 21 Okinawa Trough and beyond. *J. Geophys. Res.* 110, C05012, doi:10.1029/2004JC002494.
- 22 Chen, C.-T. A., Wang, S. L., 1998. Influence of intermediate water in the western Okinawa Trough by
 23 the outflow from the South China Sea. *J. Geophys. Res.* 103, 12683– 12688.
- 24 Chen, C.-T.A., Zhai, W., Dai, M., 2008. Riverine input and air-sea CO₂ exchanges near the Changjiang
 25 (Yangtze River) Estuary: Status quo and implication on possible future changes in metabolic status.
 26 *Cont. Shelf Res.* 28, 1476-1482.
- 27 Cutter, G.A., Cutter, L.S., 1995. Behavior of dissolved antimony, arsenic, and selenium in the Atlantic
 28 Ocean. *Mar. Chem.* 49, 295–306.

1 Cutter, G.A., Cutter, L.S., Featherstone, A.M., Lohrenz, S.E., 2001. Antimony and arsenic
2 biogeochemistry in the western Atlantic Ocean. *Deep Sea Res. Part II* 48, 2895–2915.

3 Cutter, G.A., Cutter, L.S., 2006. Biogeochemistry of arsenic and antimony in the North Pacific Ocean.
4 *Geochem. Geophys. Geosyst.* 7(5), doi: 10.1029/2005GC001159.

5 Cutter, G.A., Cutter, L.S., 1998. Metalloids in the high latitude North Atlantic Ocean: sources and
6 internal cycling. *Mar. Chem.* 61, 25-36.

7 Duan, L.Q., Song, J.M., Li, X.G., Yuan, H.M., 2010. The behaviors and sources of dissolved arsenic
8 and antimony in Bohai Bay. *Cont. Shelf Res.* 30(14), 1522-1534.

9 Duce, R. A., et al., 1991. The atmospheric input of trace species to the world ocean. *Global*
10 *Biogeochem. Cycles* 5, 193-259, doi:10.1029/91GB01778.

11 Ellwood, M. J., Maher, W.A., 2002. Arsenic and antimony species in surface transects and depth
12 profiles across a frontal zone: The Chatham Rise, New Zealand. *Deep Sea Res. Part I* 49,
13 1971-1981.

14 Featherstone, A.M., Butler, E.C., Grady, B.V.O., 2001. Meridional distribution of arsenic species in the
15 subantarctic zone of the Southern Ocean, south of Australia. *J. Geophys. Res.* 106
16 (C12),31657-31667.

17 Filella, M., Belzile, N., Chen, Y.W., 2002. Antimony in the environment: a review focused on natural
18 waters I. Occurrence. *Earth-Science Reviews* 57, 125-176.

19 Gao, Y., Arimoto, R., Duce, R.A., Zhang, X.Y., Zhang, G.Y., An, Z.S., Chen, L.Q., Zhou, M.Y., Gu,
20 D.Y., 1997. Temporal and spatial distributions of dust and its deposition to the China Sea. *Tellus*
21 *Ser. B*, 49, 172– 189.

22 Gong, G.C., Chen, Y.L.L., Liu, K.K., 1996. Chemical hydrography and chlorophyll a distribution in the
23 East China Sea in summer: implications in nutrient dynamics. *Cont. Shelf Res.* 16, 1561 – 1590.

24 Gordon, D.C., Boudreau, P.R., Mann, K.H., Ong, J.-E., Silvert, W.L., Smith, S.V., Wattayakorn, G.,
25 Wulff, F., Yanagi, T., 1996. LOICZ biogeochemical modeling guidelines. LOICZ Reports and
26 Studies 5, LOICZ, Texel, The Netherlands.

27 Guieu, C., Zhang, J., Thomas, A.J., Martin, J.M., Brun-Cottan, J.-C., 1993. Significance of atmospheric
28 fallout on the upper layer water chemistry of the North-Western Mediterranean. *J. Atmos. Chem.*
29 17, 45–60.

30 Guo, X., Miyazawa, Y., Yamagata, T., 2006. The Kuroshio onshore intrusion along the shelf break of

1 the East China Sea: the origin of the Tsushima Warm Current. *J. Phys. Oceanogr.* 36(12),
2 2205-2231, doi:10.1175/JPO2976.1.

3 He M., Wan, H., 2004. Distribution, speciation, toxicity and bioavailability of antimony in the
4 environment. *Prog. in Chem.* 16(1), 131-135. (in Chinese with English abstract)

5 Hellweger, F.L., Farley, K.J., Lall, U., Di Toro, D.M., 2003. Greedy algae reduce arsenate. *Limnol.*
6 *Oceanogr.* 48, 2275–2288.

7 Hsin, Y.C., Wu, C.R., Shaw, P.T., 2008. Spatial and temporal variations of the Kuroshio east of
8 Taiwan, 1982-2005: A numerical study. *J. Geophys. Res.* 113, C04002,
9 doi:10.1029/2007JC004485.

10 Hsu, S. C., Wong, G.T.F., Gong, G.C., Shiah, F.K., Huang, Y.T., Kao, S.J., Tsai, F., Lung, S.C.C., Lin,
11 F.J., Lin, I.I., Hung, C.C., Tseng, C.M., 2010. Sources, solubility and dry deposition of aerosol
12 trace elements over the East China Sea. *Mar. Chem.* 120, 116-127.

13 Hsu, S.C., Liu, S.C., Arimoto, R., Liu, T.H., 2009. Dust deposition to the East China Sea and its
14 biogeochemical implications. *J. Geophys. Res.* 114, D15304, doi:10.1029/2008JD011223.

15 Huang, W.W., Martin, J.M., Seyler, P., Zhang, J., Zhong, X.M., 1988. Distribution and behavior of
16 arsenic in the Huanghe (Yellow River) estuary and Bohai Sea. *Mar. Chem.* 25(1), 75-91.

17 Ichikawa, H., Chaen, M., 2000. Seasonal variation of heat and freshwater transports by the Kuroshio in
18 the East China Sea. *J. Mar. Syst.* 24, 119 – 129.

19 Krachler, M., Zheng, J.C., Fisher, D., Shotyk, W., 2008. Atmospheric Sb in the Arctic during the past
20 16,000 years: responses to climate change and human impacts. *Global Biogeochem. Cycles* 22,
21 GB1015, doi:10.1029/2007GB002998.

22 Li, D.D., 2003. Modification of atomic fluorescence determination of arsenic in natural waters, with
23 application in Jiaozhou Bay, Yellow Sea and East China Sea. Master D. thesis, Ocean University
24 of China, Qingdao. (In Chinese, with English abstract)

25 Li, Q., Yu, M., Lu, G., Cai, T., Bai, X., Xia, Z., 2011. Impacts of the Gezhouba and Three Gorges
26 reservoirs on the sediment regime in the Yangtze River, China. *J. Hydrol.* 403, 224-233.

27 Li, L., Ren, J.L., Yan, Z., Liu, S.M., Wu, Y., Zhou, F., Liu, C.G., Zhang, J., 2014. Behavior of arsenic in
28 the coastal area of Changjiang (Yangtze River) Estuary: Influences of water mass mixing, the
29 spring bloom and hypoxia. *Cont. Shelf Res.* 80(1), 67-78.

30 Liu, S. M., Zhang, J., Chen, S. Z., Chen, H. T., Hong, G. H., Wei, H., Wu, Q. M., 2003. Inventory of

1 nutrient compounds in the Yellow Sea. *Cont. Shelf Res.* 23, 1161-1174.

2 Michel, P., Boutier, B., Herbland A., Averty, B., Artigas, L.F., Auger, D., Chartier, E., 1997. Behavior of

3 arsenic on the continental shelf off the Gironde estuary: role of phytoplankton in vertical fluxes

4 during spring bloom conditions. *Oceanol. Acta* 21(2), 325-333.

5 Middelburg, J.J., Hoede, D., van der Sloot, H.A., van der Weijden, C.H., Wijkstra, J., 1988. Arsenic,

6 antimony and vanadium in the North Atlantic Ocean. *Geochim. Cosmochim. Acta* 52, 2871 –

7 2878.

8 Milliman, J.D., Meade, R.H., 1983. World-wide delivery of river sediment to the oceans. *J. Geol.* 91 (1),

9 1 – 21.

10 Millward, G.E., Kitts, H.J., Comber, S.D.W., Ebdon, L., Howard, A.G., 1996. Methylated arsenic in

11 the southern North Sea. *Estuar., Coast. Shelf Sci.* 43, 1-18.

12 Neff, J.M., 1997. Ecotoxicology of arsenic in the marine environment. *Environ. Toxicol. Chem.* 16,

13 917–927.

14 Nitani, H., 1972. Beginning of the Kuroshio, in *Kuroshio: Its Physical Aspects*, edited by Stommel, H.,

15 Yoshida, K., pp. 129 – 163, Univ.Tokyo Press, Tokyo.

16 Nriagu, J.O., 1989. A global assessment of natural sources of atmospheric trace metals. *Nature* 338:

17 47-49.

18 Oremland, R.S., Dowdle, P.R., Hoelt, S., Sharp, J.O., Schaefer, J.L., Miller, L.G., Blum, J.S., Smith,

19 R.L., Bloom, N.S., Wallschlaeger, D., 2000. Bacterial dissimilatory reduction of arsenate and

20 sulfate in meromictic Mono Lake, California. *Geochim. Cosmochim. Acta* 64, 3073-3084.

21 Oremland, R.S., Stolz, J.F., 2003. The ecology of arsenic. *Science* 300, 939-944.

22 Ren, J.L., Zhang, G.L., Zhang, J., Shi, J.H., Liu, S.M., Li, F.M., Jin, J., Liu, C.G., 2011. Distribution of

23 dissolved aluminum in the Southern Yellow Sea: Influences of a dust storm and the spring bloom.

24 *Mar. Chem.* 125, 69-81. doi:10.1016/j.marchem.2011.02.004

25 Ren, J.L., Zhang, J., Li, D.D., Cheng, Y., Liu, S.M., 2010. Behavior of dissolved inorganic arsenic in

26 the Yellow Sea and East China Sea. *Deep-Sea Res. II* 57, 1035-1046.

27 Ren, J.L., Zhang, J., Li, J.B., Yu, X.Y., Liu, S.M., Zhang, E.R., 2006. Dissolved aluminum in the

28 Yellow Sea and East China Sea – Al as a tracer of Changjiang (Yangtze River) discharge and

29 Kuroshio incursion. *Estuar., Coast. Shelf Sci.* 68, 165-174.

30 Sanders, J.G., Riedel, G.F., 1993. Trace element transformation during the development of an estuarine

1 algal bloom. *Estuaries* 16, 521-531.

2 Santosa, S. J., Wada, S., Tanaka, S., 1994. Distribution and cycle of arsenic compounds in the ocean.

3 *Appl. Organomet. Chem.* 8, 273-283.

4 Shotyk, W., Cheburkin, A.K., Appleby, P.J., Fankhauser, A., Kramers, J.D., 1996. Two thousand years

5 of atmospheric arsenic, antimony, and lead deposition recorded in an ombrotrophic peat bog

6 profile, Jura Mountains, Switzerland. *Earth Planet. Sci. Lett.* 145, E1–E7.

7 Su, J. L., Pan, Y. Q., 1987. On the shelf circulation north of Taiwan. *Acta Oceanol. Sin.* 6(Supp. 1),

8 1-20.

9 Teague, W. J., Hwang, P. A., Jacobs, G. A., Book, J. W., Perkins, H. T., 2005. Transport variability

10 across the Korea/Tsushima Strait and the Tsushima Island wake. *Deep Sea Res. II* 52(11),

11 1784-1801, doi:10.1016/j.dsr2.2003.07.021.

12 Uematsu, M., Duce, R.A., Prospero, J.M., 1985. Deposition of atmospheric mineral particles in the

13 North Pacific Ocean. *J. Atmos. Chem.* 3, 123–128, doi:10.1007/BF00049372.

14 Van der Weijden, C.H., Middelburg, J.J., De Lange, G.J., van der Sloot, H.A., Hoede, D., Woittiez,

15 J.R.W., 1990. Profiles of the redox-sensitive trace elements As, Sb, V, Mo and U in the Tyro and

16 Bannock Basins – Eastern Mediterranean. *Mar. Chem.* 31, 171–186.

17 Wan, Y.X., Ren, J.L., 2011. Determination of major antimony species (Sb(V) and Sb(III)) in natural

18 water by hydride generation atomic fluorescence spectrometry. *Mar. Sci.* 35(4), 37-43 (in Chinese

19 with English abstract).

20 Wang, H., Saito, Y., Zhang, Y., Bi, N., Sun, X., Yang, Z., 2011. Recent changes of sediment flux to the

21 western Pacific Ocean from major rivers in East and Southeast Asia. *Earth-Sci. Rev.* 108, 80-100.

22 Wang, X., He, M., Xi, J., Lu, X., 2011. Antimony distribution and mobility in rivers around the world's

23 largest mine of Xikuangshan, Huan Province, China. *Microchem. J.* 97, 4-11

24 Wang, X., Wang, J.P., Liu, C.H., Zhang, F.F., 2014. Situation analysis and sustainable development

25 strategy of antimony resources of China. *China Min. Mag.* 23(5): 9-13 (in Chinese with English

26 abstract).

27 Wong, G.T.F., Chao, S.Y., Li, Y.H., Shiah F.K., 2000. The Kuroshio edge exchange processes (KEEP)

28 study – an introduction to hypotheses and highlights. *Cont. Shelf Res.* 20, 335-347.

29 Wurl, O., Zimmer, L., Cutter, G.A., 2013. Arsenic and phosphorus biogeochemistry in the ocean:

30 Arsenic species as proxies for P-limitation. *Limnol. Oceanogr.* 58, 729-40.

1 Xiao, X.Y., Chen, T.B., Liao, X.Y., Wu, B., Yan, X.L., Zhai, L.M., Xie, H., Wang L.X., 2008. Regional
2 distribution of arsenic contained minerals and arsenic pollution in China. *Geograph. Res.* 27(1),
3 201-212 (in Chinese with English abstract).

4 Yao, Q.Z., Zhang, J., Qin, X.G., Xiong, H., Dong, L.X., 2006. The behavior of selenium and arsenic in
5 the Zhujiang (Pearl River) Estuary, South China Sea. *Estur., Coast. Shelf Sci.* 67(1-2), 170-180.

6 Yao, Q.Z., Zhang, J., Wu, Y., Xiong, H., 2007. Hydrochemical processes controlling arsenic and
7 selenium in the Changjiang River (Yangtze River) system. *Sci. Total Environ.* 377(1), 93-104.

8 Zhang, J., Liu, S.M., Ren, J.L., Wu, Y., Zhang, G.L., 2007. Nutrient gradients from the eutrophic
9 Changjiang (Yangtze River) Estuary to the oligotrophic Kuroshio waters and re-evaluation of
10 budgets for the East China Sea Shelf. *Progr. in Oceanogr.* 74, 449-478.

11 Zhang, J., Su, J. L., 2004. Nutrient dynamics of the China Seas: The Bohai Sea, Yellow Sea, East
12 China Sea and South China Sea. In: Robinson, A., Brink, K. (Eds.), *The Sea*. Press of Harvard
13 University, USA. 14: Chapter 14-17.

14 Zhang, X.Z., Ren, J.L., Liu, Z.G., Fan, X.P., Liu, C.G., Wu, Y., 2014. Distributions and influencing
15 factors of total dissolved inorganic antimony in the coastal area of Zhejiang and Fujian. *Environ.*
16 *Sci.* 35(2): 547-554. (in Chinese with English abstract)

17

Captions of figures:

Figure 1. Sampling locations of the East China Sea for the May 2011 cruise, with illustrations of circulation regimes including Changjiang Diluted Water (CDW); Kuroshio Water (KW) and Taiwan Strait Warm Water (TSWW). Abbreviation of TAS represents Taiwan Strait. Sections of PN and KWL are highlighted as bold dashed lines.

Figure 2. Horizontal distributions of temperature, salinity and SPM (mg/l) in the surface and bottom layer of the East China Sea.

Figure 3. Relationships between temperature and salinity of seawater for sections PN and KWL. Isopycnals are shown. CDW, the Changjiang Diluted Water; TSWW, the Taiwan Strait Warm Water; KSW, the Kuroshio Surface Water; KSSW, the Kuroshio Subsurface Water; KIW, the Kuroshio Intermediate Water; SMW, the Shelf Mixed Water. The definitions of the water masses are based on Gong et al. (1996) and Ichikawa and Chaen (2000).

Figure 4. Horizontal distributions of TDIA_s, As (III), TDIS_b and Sb (III) (nM) in the surface and bottom layer of the East China Sea.

Figure 5. Vertical profiles of temperature, salinity, SPM (mg/l), TDIA_s (nM), As(III) (nM) and TDIS_b (nM) at PN section in the East China Sea. Note the difference in scales of depths above and below 150 m.

Figure 6. Vertical profiles of temperature, salinity, SPM (mg/l), TDIA_s (nM), As(III) (nM) and TDIS_b (nM) at KWL section in the East China Sea.

Figure 7. Vertical profiles of temperature, salinity, TDIA_s, As(III) and phosphate at stations C4 and C7 in the East China Sea.

Figure 8. Relationship between As(III)/TDIA_s ratio and phosphate in spring of 2011 in the East China Sea. Data are separated into three groups: coastal region, indicates the stations located within 50 m isobaths in the ECS and 20 m isobaths in the YS; Northern Shelf and Southern Shelf, indicate the stations located at the north and south of latitude 28°N in the ECS shelf and shelf break area, respectively. According to the chlorophyll-sensing satellite images from NASA

(http://oceancolor.gsfc.nasa.gov/cgi/l3?ctg=Standard&sen=A&prd=CHL_chlor_a&per=DAY&date=1May2009&res=4km&num=24), spring blooms were occurred at the coastal and

1 northern ECS during April 17 and 27. Dashed line is the regression between As(III)/TDIAs
2 and phosphate for the group of Northern Shelf.
3 Figure 9. Vertical profiles of TDISb at stations G8, ED, D9, DC in the East China Sea. Station 1
4 (34.467°N, 146.99°E, locates at the northern edge of the subtropical gyre in the Kuroshio
5 Current, western North Pacific, [Cutter and Cutter, 2006](#)) are redraw for the comparison.
6

Fig. 1

1

2

3 Fig. 2

4

Fig. 3

1

2

3 Fig. 4

4

1

2

3 Fig. 5

4

1

2

3 Fig. 6

4

1

2

3 Fig. 7

4

1

2 Fig. 8

3

Fig. 9

1 Table 1
2 The ranges and average (in bracket) concentrations of temperature, salinity, SPM, TDIAAs, arsenite,
3 TDISb and Sb(III) and the ratios of As(III)/TDIAAs and Sb(III)/TDISb in the surface and bottom layer of
4 the East China Sea covered by the cruise of spring 2011

Laye r	Tempera ture	Salinity	SPM (mg/l)	TDIAAs (nM)	As(III) (nM)	As(III)/T DIAAs	TDISb (nM)	Sb (III) (nM)	Sb(III)/T DISb
Surfa ce	14.83-26 .33 (20.2±3. 47)	24.376-34. 585 (32.210±2. 290)	1.2-252. 3 (14.9±36 .8)	8.7-23. 9 (15.3± 2.7)	0.33-8.5 2 (1.83±1 .82)	0.02-0.56 (0.13±0.1 3)	1.16-4.9 8 (2.13±0 .82)	BDL-0. 18 (0.05±0 .05)	0-0.10 (0.03±0.0 3)
Bott om	4.00-23. 92 (15.71±4 .62)	24.212-34. 904 (33.128±1. 985)	1.6-856. 2 (125.8±4 6.3)	11.4-2 3.2 (16.8± 2.5)	0.19-1.9 5 (0.45±0 .15)	0.01-0.06 (0.03±0.0 1)	0.84-4.7 6 (1.77±0 .72)	BDL-0. 27 (0.07±0 .07)	0-0.21 (0.05±0.0 5)

5 BDL, below the detection limit.

6

1 Table 2

2 Comparison of the dissolved arsenic and antimony concentrations between ECS and world regions

Region	TDIAs (nM)	As (III) (nM)	TDISb (nM)	Sb (III) (nM)	Reference
ECS	2.5-24.1 (16.2)	0.15-8.52 (0.92)	0.71-4.98 (1.84)	BDL-0.30 (0.08)	this study
(below 500 m)	15.4-24.1 (19.7)	0.22-0.44 (0.32)	1.46-2.54 (1.80)	BDL-0.27 (0.09)	
North Pacific	14.6±1.2 (surface)	BDL-0.7 (0.10) (deep water)	1.16±0.35 (surface)	BDL-1.0	Cutter and Cutter, 2006
	24.2±0.4 (deep water)		0.83±0.08 (below 2500 m)		Andreae, 1979
South Pacific (surface)	18±2				Ellwood and Maher, 2002
Atlantic Ocean (surface)	16.3±2.1	0.45	1.87±0.38 (high latitude)		Cutter and Cutter, 1998; Middelburg et al., 1998
			1.25±1.44 (equatorial)		Cutter et al., 2001
Western Atlantic (IOC)					Cutter et al., 2001
Stn.10 (southernmost)					
Upper layer		0.35			
NADW (2200-3200 m)	21.2±1.7	0.09 (700m-bottom)	0.91±0.12		
AABW (3950-4460 m)	20.4±0.4		0.53±0.05		
Stn.8 (Brazil Strait)					
upper thermocline		0.37	1.46	0.02	
AAIW (700-850 m)		0.09	0.60	BDL	
UCDW (900-1500 m)		0.10	0.68	BDL	
NADW (1900-3300 m)	19.4±0.3		0.72±0.15	BDL	
AABW (4700-5200 m)	19.3±0.3		0.80±0.13	BDL	
Stn.RF (Middle of the deep Romanche Fracture zone)					
20-m mixed layer		0.29	2.2	0.01 (max. of upper 200m)	

AAIW (600-800 m)	20.3±1.7	0.06 (deep water)	0.87±0.21	BDL	
NADW (1000-4000 m)	19.6±1.6		1.07±0.27	BDL	
AABW (4800-5300 m)	20.4±0.8		1.13±0.07	BDL	
Stn.6 (northernmost)					
surface		1.2	1.52		
AAIW (600-900 m)		0.08	1.11	BDL	
NADW (1700-4200 m)	20.2±0.6	BDL	1.07±0.07	BDL	
AABW (4500-4600 m)	20.2±0.6	BDL	1.27±0.01	BDL	
Eastern Atlantic Ocean					Cutter and Cutter, 1995
surface	12.9±1.8		1.12±0.25		
2000-4600 m	19.1±0.7		1.08±0.13		
Southern Ocean	21.1-23.0 (22.2±1.3, surface)	0.04			Featherstone et al., 2001;
	24.1±0.5 (below 1000 m)				Santosa et al., 1994
Amazon River plume	9.83	0.7-1.9	0.5-1.5	0.03-0.06	Cutter et al., 2001
Amazon River (3°13'S, 59°0.2'W)	2.8		0.25		Cutter et al., 2001

- 1 AABW: Antarctic Bottom Water; AAIW: Antarctic Intermediate Water; NADW: North Atlantic Deep
- 2 Water; UCDW: Upper Circumpolar Deep Water

1 Table 3

2 Budgets of dissolved antimony in the ECS

Transport	Salinity ^a	Water fluxes ^a (Sv)	Sb (nM)	Sb flux (mol s ⁻¹)	Reference
Input					
Changjiang	0	0.036–0.046	10.1–12.6 (11.4)	0.36–0.58 (0.48) ^b	This study
Kuroshio water					
KSW	34.2–34.8	0.84–0.94	1.48–2.47 (1.78)	1.07–2.27 (1.53) ^c	This study
KSSW			1.20–2.40 (1.70)		
TSWW	33.6–34.2	1.88–3.16	0.98–2.06 (1.68)	1.84–6.51 (3.07)	This study
Atmospheric					
dry	dry deposition velocity (cm s ⁻¹)		2.0±1.5		Hsu et al., 2009
	aerosol Sb concentration (ng m ⁻³)		1.57±1.08 (East China Sea)	0.050±0.026 ^d	Hsu et al., 2010
total				0.18±0.09 ^e	
Output					
Yellow Sea	31.15–32.75	0.009	0.58–3.25 (1.74)	0.0052–0.029 (0.016)	This study
Shelf Mixed Water	31.15–34.30	2.77–4.16	0.63–2.74 (1.50)	1.74–11.4 (5.20)	This study

3 ^a The salinity and water fluxes of the water masses are cited from [Zhang et al. \(2007\)](#);

4 ^b Nearly 85.9% of the discharge empties into the ECS Shelf ([Liu et al., 2003](#));

5 ^c Assume that the incursion of the Kuroshio from north of Taiwan mainly compose by the KSW (i.e., 25%) and the KSSW (i.e., 75%);

6 ^d Estimated according to the aerosol samples collected at different sites and average solubility of Sb in dry deposition is 36±7% ([Hsu et al., 2010](#)).

7 ^e Estimated according to the average ratio between seasonal variations in atmospheric deposition through dry and wet deposition to northern Taiwan between 2002 and
8 2006, with the result of 27% and 73%, respectively. Assume that the solubilities of Sb in dry and wet deposition are same ([Hsu et al., 2009](#)).