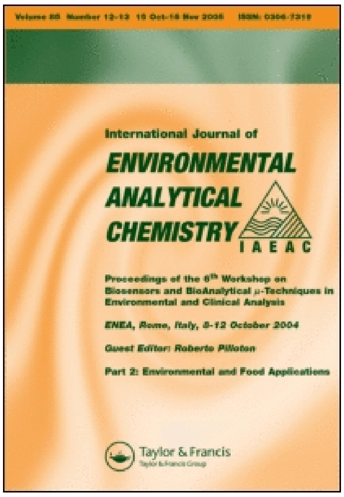

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MERCURY SPECIATION IN CHINA'S COASTAL SURFACE SEAWATERS

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Mercury contamination of ocean ecosystems is one of many problems in the global environment. In this paper, mercury speciation for surface seawaters sampled from nine coastal sites of China was performed. Speciation analysis of total particulate mercury $(Hg_T)_P$, total dissolved mercury $(Hg_T)_D$, monomethylmercury $(MMHg)_D$, dimethylmercury $(DMHg)_D$, mercuric ion $(Hg^{2+})_D$ and mercuric chlorocomplexes $(HgCl_3^-$ and $HgCl_4^{2-})_D$ was carried out by cold vapor atomic fluorescence spectrometry (CVAFS) after separation and preconcentration with thiol cotton fiber (TCF) and anion-exchange resin columns. The concentration of $(Hg_T)_D$ ranged from 25.3 to 41.1 ng/L. The concentration of dissolved inorganic mercury was in the range of 12.8–24.7 ng/L, which averaged 55.9% of the total dissolved mercury. Dissolved mercuric chlorocomplexes $(HgCl_3^-$ and $HgCl_4^{2-})_D$ appeared to be the principal speciation, averaging 45.7% of total dissolved mercury. The concentration of $(MMHg)_D$ was higher in coastal seawaters collected in Beidaihe (2.55 ng/L) and Huludao (2.36 ng/L). In other costal water samples, the concentration of $(MMHg)_D$ ranged from 0.23 to 0.86 ng/L. A significant inverse correlation was observed between $(MMHg)_D$ and dissolved oxygen content. Labile inorganic mercury (II) was probably the most likely substrate for mercury methylation. The highest concentration of dissolved DMHg (0.136 ng/L) was detected in seawater sampled in Xiamen. Particulate mercury constituted 51–90% of the total mercury. The enrichment ability of the suspended particle matter for dissolved mercury was calculated to be 0.5×10^3 to 2.1×10^3. The particulate mercury varied from 12 to 63 ng/g, and the variations were positively correlated with the suspended particle matter concentrations, whereas a negative correlation was observed with salinity. Particulate mercury originated mainly from river inputs.

Keywords: Mercury; Speciation; Coastal surface seawater; Thiol cotton fiber

INTRODUCTION

It is well known that among the toxic trace metals, mercury is one of the most hazardous pollutants in the marine environment. Although all forms of mercury (e.g. elemental, inorganic and organic) can have adverse health effects at sufficiently high doses, their toxicities differ depending on the form. Compared with other mercury

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species, organic mercury compounds are of particular concern because of their enhanced toxicity, lipophilicity, efficient bioaccumulation, volatility and long-term elimination from tissues [1–3]. For example, mercury poisoning caused mainly by monomethylmercury (MMHg) has been observed in marine life and humans in Minamata, Japan [4], in marine birds in Sweden [5] and in humans in Iraq [6]. Consumption of marine fish and seafood products is the principal pathway by which humans are exposed to the very toxic organo-mercurial, MMHg. There is an urgent need for more knowledge and understanding of the marine biogeochemical cycling of mercury, and the most important issue is to understand the distribution and speciation of mercury in seawater.

In recent decades, many efforts have focused on mercury speciation in ocean waters. Mason and Fitzgerald [7–9] thoroughly studied the distribution, speciation and biogeochemical cycling of mercury in the equatorial Pacific Ocean. Coquery and Cossa [10] determined mercury speciation in surface waters of the North Sea including the Elbe estuary. The concentrations of MMHg and DMHg were determined in the Antarctic and Arctic Ocean water as well as seawater collected from other remote areas (South Atlantic and South Pacific) [11]. Mercury speciation analysis was also performed in coastal waters sampled from the Spanish Cantabric Sea [12], South Bight of the North Sea [13] and Plymouth, UK [14,15]. Mercury reaches the sea by different routes. The major routes are from rivers, so a number of studies have been carried out on the behavior and speciation of mercury in the Gironde estuary [16], Scheldt estuary [17,18] and Adour estuary [19], amongst others.

Dissolved mercuric ion $(Hg^{2+})_D$ and mercuric chlorocomplexes ($HgCl_3^-$ and $HgCl_4^{2-})_D$ are experimentally defined as dissolved 'reactive' or 'easily reducible' mercury $(Hg_R)_D$. The concentration and rate of supply of labile ionic Hg substrate, with ($HgCl_3^-$ and $HgCl_4^{2-})_D$ as the greatest component, determine the rate of mercury methylation in the upper ocean [9]. However, speciation analysis of dissolved mercuric ion $(Hg^{2+})_D$ and mercuric chlorocomplexes ($HgCl_3^-$ and $HgCl_4^{2-})_D$ in seawater has been scarcely reported.

Mercury species in seawater (normally present at low levels: ng/L to sub-ng/L) need to be preconcentrated before determination by atomic spectrometry. The traditional approaches include Carbotrap^R (a carbon absorbent) trapping of $(DMHg)_D$ and $(MMHg)_D$ (after derivatization using sodium tetraethylborate), gold or gold wool trapping of dissolved gaseous mercury and $(Hg_R)_D$ (after reduction using $SnCl_2$) [9,16], and cold trapping of $(MMHg)_D$ (after derivitization using sodium tetraethylborate) [11], $(Hg^{2+})_D$ and $(MMHg)_D$ (by on-line hydride generation, cryogenic trapping, gas-chromatography separation and AFS detection) [19]. Solid-phase extraction is another successful method by which to preconcentrate mercury compounds. 2-Mercaptoethanol-modified C_{18} Sep-pack cartridges were used for off-line preconcentration of $(Hg^{2+})_D$ and $(MMHg)_D$ in seawater before their determination by cold vapor atomic absorbance spectrometry coupled with vesicle-enhanced high-performance liquid chromatography [12]. A dithiocarbamate (Dithiochel) resin could also preconcentrate $(Hg^{2+})_D$ and $(MMHg)_D$ in seawater before determination by inductively coupled plasma mass spectrometry coupled with liquid-chromatographic separation [14]. Preconcentration of $(Hg^{2+})_D$ and $(MMHg)_D$ on the TCF was a traditional concentration technique for determination in natural waters [20–23], but as far as we know, few efforts have been made to preconcentrate $(Hg^{2+})_D$ and $(MMHg)_D$ in seawater matrix using TCF.

The aim of the present study is to evaluate the distribution of various mercury species in coastal seawaters of China, including dissolved mercuric ion $(Hg^{2+})_{D,}$ mercuric chlorocomplexes $(HgCl_3^-$ and $HgCl_4^{2-})_D$, dissolved monomethylmercury $(MMHg)_D$ and dimethylmercury $(DMHg)_D$, total dissolved mercury $(Hg_T)_D$ and total particulate mercury $(Hg_T)_P$. In this paper, the experimental conditions of preconcentration using TCF are also optimized. The results of our survey in coastal seawaters of China are compared with previous monitoring reports from China, as well as other data from other studies undertaken in the different harbors, estuaries, and oceans of the world. The distribution of different mercury species in the coastal seawaters of China is discussed with respect to the variations in salinity, concentrations of dissolved oxygen and suspended particulate matter of the sampled seawaters.

EXPERIMENTAL

Sample Collection

Surface seawater samples were collected from nine coastal sites (shown in Fig. 1) along the northern, eastern and southern coast of China in October 2002. Most of the cities are economically developed. The sample localities are situated approximately 10 miles from the coast and at a depth of 1 m. Samples were processed immediately

FIGURE 1 Location of sampling stations. (1) Dalian (38° 46.7′ N 122° 35.7′ E), (2) Yingkou (39° 55′ N 121° 56′ E), (3) Huludao (40° 49′ N 120° 06′ E), (4) Beidaihe (39° 24′ N 118° 33′ E), (5) Tianjin (38° 59′ N 117° 42′ E), (6) Yantai (37° 32.8′ N 121° 24′ E), (7) Qingdao (35° 58.5′ N 120° 18.3′ E), (8) Xiamen (24° 28.8′ N 118° 04.2′ E) and (9) Guangzhou (22° 26′ N 112° 27′ E).

after collection. Sample collection and treatment were performed using clean techniques, including the use of a laminar air flow bench to avoid sample contamination, and polyethylene gloves were used for handling operations. The Teflon® bottles (5 L) used to collect seawater were rinsed sequentially with tap water, neutral detergent and Milli-Q water; this was followed by soaking in 1 : 1 HNO_3 for 3 days, then 10% HNO_3 for another 3 days at 50°C, and finally several rinses with Milli-Q water prior to use. Cleaned Teflon® bottles were filled with Milli-Q water acidified with HCl (1% v/v, Suprapur® Merck) and stored in double polyethylene bags until use. Before being filled, the sampling bottles were rinsed three times with the surface seawater. Water samples were filtered at the site through an acid-precleaned Millipore cellulose membrane with a pore size of 0.45 µm. Filtered samples were collected in 5-L Teflon® bottles and stored at 4°C. Filters were stored at −18°C in tightly sealed polystyrene Petri dishes before analysis of total particulate mercury $(Hg_T)_P$. Samples were collected separately for the measurement of dissolved oxygen.

Sample Analysis

Samples were analyzed for $(Hg_T)_P$, $(Hg_T)_D$, $(HgCl_3^-$ and $HgCl_4^{2-})_D$, $(Hg^{2+})_D$, $(MMHg)_D$ and $(DMHg)_D$. All Hg species, except $(HgCl_3^-$ and $HgCl_4^{2-})_D$, were detected by CVAFS (Beijing Rayleigh Instrument Co., AF–610A) after transformation to Hg^{2+}, which was then reduced to Hg^0 by KBH_4. $(HgCl_3^-$ and $HgCl_4^{2-})_D$ was measured spectrophotometrically (Shimadzu UV-265 spectrophotometer) after extraction with dithizone. All reagents were of guaranteed grade or spec-purity grade.

$(Hg_T)_P$ Analysis

Concentrations of $(Hg_T)_P$ were determined after the decomposition of suspended particles with 5 mL HNO_3 : HCl (9 : 1, v/v; Suprapur® Merck) in Teflon® (PFA) reactors through heat for 1 h at 50°C in an aluminum block [10]. Solutions were diluted with Milli-Q water, and then Hg was determined by CVAFS.

$(Hg_T)_D$ Analysis

A portion of 90 mL of filtered water sample was oxidized by 10 mL of 0.05 mol/L BrCl solution [24] at room temperature for 2 h [25]. Before the Hg concentration was determined by CVAFS, the excess of BrCl was neutralized with 50 µL of 20% w/v $NH_2OH \cdot HCl$ solution.

$(HgCl_3^-$ and $HgCl_4^{2-})_D$ Analysis

One liter of filtered water sample was acidified to 0.1 mol/L with nitric acid and then passed through a strongly basic type anion exchange resin (Amberlite IRA-410 Chloride, effective size: 0.44 mm, Aldrich) column (0.1 g of resin used) at a flow rate of 5 mL/min. After washing with 25 mL of Milli-Q water, $(HgCl_3^-$ and $HgCl_4^{2-})$ adsorbed on the column were eluted at a flow rate of 1 mL/min with 20 mL of a 1 : 5 solution of 45% w/w perchloric acid and ethyl acetate. After removal of ethyl acetate, mercury was extracted as the dithizone complex from the dilute perchloric acid into chloroform, back-extracted into 5 mol/L hydrochloric acid and finally measured spectrophotometrically after a further extraction with dithizone [26].

$(Hg^{2+})_D$, $(MMHg)_D$ and $(DMHg)_D$ Analysis

Preconcentration of $(Hg^{2+})_D$ and $(MMHg)_D$ was adopted with TCF, which was prepared according to Yu *et al.* [27]. A TCF enrichment installation consisted of a 250-mL Pyrex separatory funnel vertically fastened at the low part to a glass tube, 6–8 mm in diameter and 80 mm in length, one end of which was thinned and in which 0.1 g of TCF had been added (the length of the TCF column was 30–40 mm). The sample flow rate was adjusted using a peristaltic pump (France, Gilson, No. 58060).

Briefly, to determine $(Hg^{2+})_D$, $(MMHg)_D$ and $(DMHg)_D$ in surface seawaters, 1000 mL of filtered water was adjusted to a pH of < 1 with HCl followed by the addition of 0.1 mL 1 mol/L $CuSO_4 \cdot 5H_2O$. After thorough mixing, the water sample was maintained at room temperature for 10 min, during which time, monomethyl mercury associated with the anion cluster was converted to monomethyl mercury chloride. The seawater sample was adjusted to pH 3 and then passed through the TCF column at a flow rate of 7 mL/min. After washing with 25 mL of Milli-Q water, MMHg and Hg^{2+} retained on the column were eluted at a flow rate of 1 mL/min using 4 mL of 2 mol/L HCl for the desorption of MMHg first and then 5 mL of 3 mol/L HCl–5% KBr w/v for Hg^{2+} desorption. The Hg concentrations in the eluants were determined by CVAFS. MMHg was oxidized by 0.1 mL of 5% $KMnO_4$ w/v prior to determination to transform MMHg to Hg^{2+}. The excess of $KMnO_4$ was reduced by 20% $NH_2OH \cdot HCl$ w/v before determination.

The filtrate was collected and acidified with HCl to make the final concentration of HCl of 2 mol/L. After adding 0.0248 g $Na_2S_2O_3 \cdot 5H_2O$ to 1000 mL of effluent to make up the final concentration of $Na_2S_2O_3$ to 1.0×10^{-4} mol/L, the solution was maintained at room temperature for 1.5 days. During this operation procedure, DMHg remaining in the filtrate (which could not be adsorbed on TCF) was converted to MMHg and determined in the same way as MMHg.

Dissolved Oxygen, Salinity and Suspended Particulate Matter

Dissolved oxygen (DO) was determined with an 862A Analyzer (Orion Research, Inc. USA). Salinity was recorded *in situ* with a Conductivity Probe (HACH Model 50161 UK). Concentrations of suspended particulate matter (SPM) were determined gravimetrically after filtration of water aliquots on pre-weighed Millipore cellulose membranes (0.45 μm).

RESULTS AND DISCUSSION

Optimization of Conditions for $(Hg^{2+})_D$ and $(MMHg)_D$ Preconcentration Through TCF

The experimental parameters, such as the fiber capacity, effect of pH, flow rate, volumes of sample and eluant, eluant type and concentration, matrix interference, blank and detection limits, were carefully optimized with Hg^{2+} and MMHg in an artificial seawater matrix (Na^+ 20 000 mg/L, K^+ 500 mg/L, Mg^{2+} 2500 mg/L, Ca^{2+} 500 mg/L, added as their chlorides [28]). The results are shown in Fig. 2. As can be seen, at pH 3 and a sample flow rate of 7 mL/min, TCF could quantitatively adsorb Hg^{2+} and MMHg from 1000 mL of artificial seawater simultaneously. Then, Hg^{2+} and MMHg could be desorbed from the TCF column separately by using different eluants in sequence. MMHg was eluted by 4 mL of 2 mol/L HCl first, and then 5 mL of 3 mol/L HCl–5% KBr w/v was used for the following desorption of Hg^{2+}. The preconcentration factors were 200 and 250 for Hg^{2+} and MMHg, respectively.

The capacities of the TCF for Hg^{2+} and MMHg were found to be 28 and 50 mg/g, at pH 3, respectively. It can be seen that the capacity of the fiber is high enough for the preconcentration of $(Hg^{2+})_D$ and $(MMHg)_D$ from seawater. An eluant of 3 mol/L HCl–5% w/v KBr was chosen for elution of Hg^{2+}. The concentrations of acid and salt were lower than the commonly used eluant (6 mol/L HCl solution saturated with NaCl).

To illustrate the possibility of preconcentrating trace Hg^{2+} and MMHg from high-salt matrices using TCF adsorbent, synthetic solutions of 1000 mL of artificial seawater (Na^+ 20 000 mg/L, K^+ 500 mg/L, Mg^{2+} 2500 mg/L, Ca^{2+} 500 mg/L, added as chlorides)

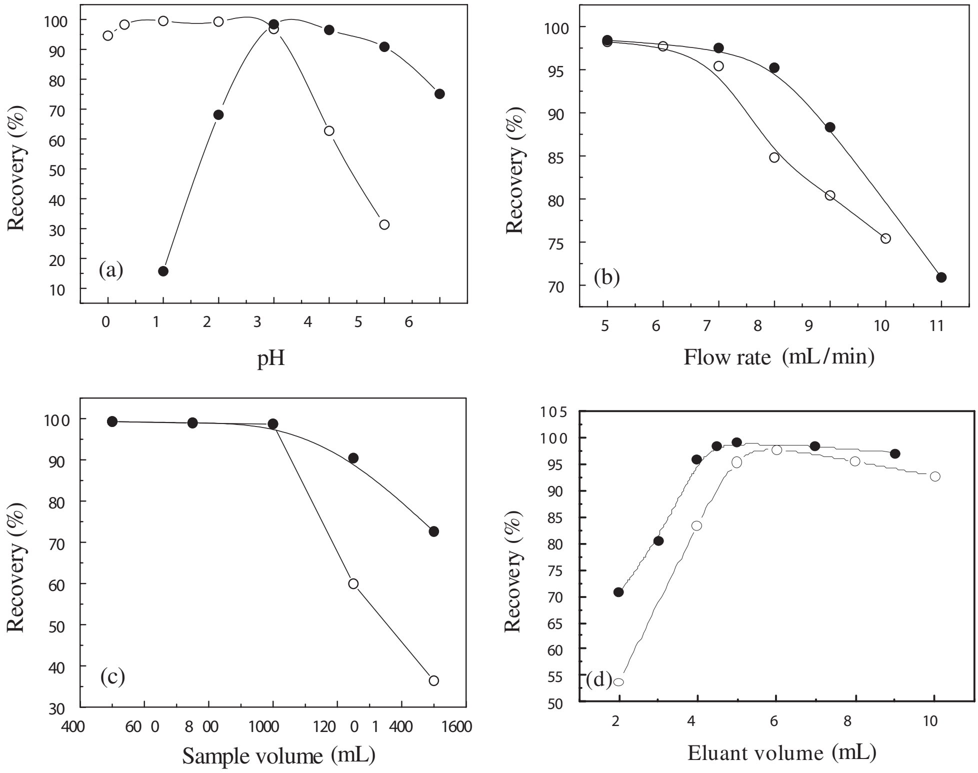

FIGURE 2 Effect of (a) sample pH (sample volume: 100 mL), (b) sample flow rate (sample volume: 1 L) and (c) sample volume on concentration efficiency of Hg^{2+} (○) and MMHg (●) (Hg^{2+}: 3 μg/L, eluant: 5 mL of 3 mol/L HCl–5% w/v KBr; MMHg: 1 μg/L, eluant: 4 mL of 2 mol/L HCl), and (d) elution efficiency of Hg^{2+} (○) and MMHg (●) as a function of eluant volume (sample volume: 1 L, concentration of Hg^{2+}: 3 μg/L, MMHg: 1 μg/L). All experiments were done in triplicate.

were used as samples. The results obtained in these experiments demonstrated that large amounts of alkali and alkaline earth metals in the sample have no significant effect on the recoveries of the Hg^{2+} and MMHg (recoveries varied between 95 and 106%). This study verified that the TCF adsorbent could separate matrices effectively. The blank values, which were obtained by performing the preconcentration procedure using 1000 mL of Milli-Q water as the sample, were 2.41 ng/L of Hg^{2+} and 0.19 ng/L of MMHg, respectively [28].

Method Accuracy

The method accuracy was checked using the standard addition method for $(Hg^{2+})_D$, $(MMHg)_D$, $(DMHg)_D$ and available reference material for suspended particulate mercury $(Hg_T)_P$. The results are shown in Tables I and II, from which we can see that the recommended method is satisfactorily reliable.

Precision and Detection Limit

The precisions for $(Hg_T)_P$, $(Hg_T)_D$, $(Hg^{2+})_D$, $(MMHg)_D$ and $(DMHg)_D$ analyses ($n = 5$) were better than 10%, and the precision for $(HgCl_3^-$ and $HgCl_4^{2-})_D$ analysis was better than 15%.

Defined as three times the standard deviation of the blank, the detection limits of $(Hg_T)_P$, $(Hg_T)_D$, $(HgCl_3^-$ and $HgCl_4^{2-})_D$, and $(DMHg)_D$ were 2.3, 1.4, 3.8 and 0.126 ng/L, respectively. The detection limits of $(Hg^{2+})_D$ and $(MMHg)_D$ were 0.42 and 0.20 ng/L, respectively, which were calculated [28] based on three times the standard deviation of 11 runs of the blank solution and the concentration factor of 200 for Hg^{2+} and 250 for MMHg.

Distribution of Different Mercury Speciations Along the Coast of China

The concentrations of different mercury speciations, including $(Hg^{2+})_D$ and $(HgCl_3^-$ and $HgCl_4^{2-})_D$, $(MMHg)_D$ and $(DMHg)_D$, $(Hg_T)_D$ and $(Hg_T)_P$, in surface seawaters collected from nine coastal sites of China are listed in Table III, together with the DO contents, salinities and concentrations of SPM of the water samples.

Salinity, Suspended Particulate Matter and Dissolved Oxygen

The salinity ranged from 24.7 to 39.0‰. The concentrations of SPM varied between 0.53 and 6.05 mg/L. As the salinity increased, the concentrations of SPM generally decreased. The linear regression between the concentrations of SPM and the salinity was significant ($r = -0.88$, $P < 0.01$; Fig. 3a). The concentrations of DO averaged 5.63 ± 0.25 mg/L. DO was also negatively correlated with salinity ($r = -0.69$, $P < 0.05$; Fig. 3b).

Concentrations and Distribution of Dissolved Total and Inorganic Mercury

Dissolved total mercury concentrations $[(Hg_T)_D]$ ranged from 25.3 to 41.1 ng/L, with an average concentration of 32.5 ± 3.9 ng/L. A trend of increasing concentration of $(Hg_T)_D$ with decreasing salinity was observed for the whole data set. The

TABLE I Recovery of Hg^{2+}, MMHg and DMHg added to seawater samples (sample volume: 1000 mL, eluant volume: 5 mL for Hg^{2+} and 4 mL for MMHg)[a] (%)

Analyte (ng/L)	*Huludao seawater*				*Qingdao seawater*				*Xiamen seawater*				*Guangzhou seawater*			
	Found	*Added*	*Total found*	*Recovery*	*Found*	*Added*	*Total found*	*Recovery*	*Found*	*Added*	*Total found*	*Recovery*	*Found*	*Added*	*Total found*	*Recovery*
Hg^{2+}	3.58	3.60	7.68	107	2.17	2.20	4.50	103	8.39	8.40	16.62	99	2.84	2.90	5.68	99
MMHg	2.36	2.40	4.66	98	0.23	0.25	0.45	94	0.49	0.50	0.98	99	0.40	0.40	0.76	95
DMHg	0.097	0.13	0.22	98	n.d.	0.15	0.146	97	0.136	0.140	0.265	96	0.014	0.13	0.135	94

[a] Four surface seawaters were selected. There were five measurements for each sample, and the RSDs were less than 10%.

TABLE II Accuracy of the method used for $(Hg_T)_P$ analysis

Standard reference material[a]	*Determined* (μg/g)	*Certified* (μg/g)
Geochemical standard reference sample, Drainage Sediment, GSD-10, China	0.26 ± 0.03	0.28 ± 0.04
Marine sediment reference material, BCSS-1, National research council, Canada	0.121 ± 0.015	0.129 ± 0.012

[a] Five measurements for each sample.

linear regression was statistically significant ($r = -0.57$, $P = 0.10$; Fig. 4a). The relationship was greatly improved ($r = -0.97$, $P < 0.01$) if the sample from Huludao was omitted. Huludao is an industrial city with a long history and has many kinds of plants, including a chlor-alkaline plant, petroleum refinery, chemical engineering factory, shipyard and zinc refinery. Thus, compared with other cities, much more mercury reaches the sea as a result of considerable industrial blow-off from Huludao.

Our data are not significantly different from the level encountered in Sutton Harbour, Plymouth (24 ± 5 to 54 ± 10 ng/L) [15]. However, in contrast to the range of concentrations reported for the equatorial Pacific Ocean (0.008–0.065 ng/L) during the NOAA MB-90-O1-RITS cruise of the Malcolm Baldridge from 3 January to 18 February 1990, the concentrations from our report are much higher. The concentrations of $(Hg_T)_D$ found in the North Sea (0.18–0.96 ng/L) [10], in the estuary of Scheldt (0.5–3.0 ng/L; dissolved Hg species show large seasonal variations essentially controlled by the redox conditions in the estuary) [17] and in Adour (France, below the detection limit to 7.81 ± 0.41 ng/L) [19] were all lower than those in the present study. But from comparisons with the data reported in 'Records of China Bay' (0.02–0.24 μg/L) [29] and 'Marine Chemistry of the Bohai Sea, the Yellow Sea and the East China Sea' (0.014–1.830 μg/L) [30], the concentration of $(Hg_T)_D$ has clearly decreased over the last decade.

Dissolved inorganic mercury in seawater is mainly composed of dissolved mercuric ion $(Hg^{2+})_D$ and its chlorocomplexes $(HgCl_3^-$ and $HgCl_4^{2-})_D$. In contrast, an experimentally defined fraction of the total dissolved mercury, dissolved 'reactive' or 'easily reducible' mercury $(Hg_R)_D$, consists mostly of inorganic mercury. In this study, the concentrations of $(Hg^{2+})_D$ ranged from 2.00 to 8.90 ng/L. This level is not significantly different from the level encountered in the Adour estuary (1.15 ± 0.32 to 9.88 ± 0.02 ng/L) [19]. However, our data are lower than the range of concentrations reported for coastal water sampled in Plymouth Sound (21–28 ng/L) [14]. In this work, the concentrations of $(HgCl_3^-$ and $HgCl_4^{2-})_D$ ranged from 8.97 to 18.24 ng/L. The concentrations of dissolved inorganic mercury, $(Hg_{Inorg})_D = (Hg^{2+})_D + (HgCl_3^-$ and $HgCl_4^{2-})_D$, ranged from 12.78 to 24.71 ng/L, with an average concentration of 17.74 ± 2.81 ng/L, and represented on average 16.75% (4.23–49.43%) of the Hg_T $(Hg_T = (Hg_T)_D + (Hg_T)_P)$. The percentage of $(Hg_{Inorg})_D$ in Hg_T was positively correlated with salinity ($r = +0.74$, $P < 0.05$; Fig. 4b).

In total dissolved mercury $(Hg_T)_D$, the content of $(Hg_{Inorg})_D$ varied from 36.2 to 81.3% with an average of 55.9%. Considering the low percentage of $(Hg^{2+})_D$ in $(Hg_{Inorg})_D$ (averaging 25.7%), it can be deduced that mercuric chlorocomplexes appeared to be the principal Hg species in total dissolved mercury $(Hg_T)_D$ (averaging 45.7%) and that dissolved Hg is not strongly bound to organic matter. In seawater

TABLE III Dissolved and particulate mercury concentrations in surface seawaters sampled in nine Chinese coastal cities

Sampling site	*DO* (mg/L)	*Salinity* (‰)	*SPM* (mg/L)	$(Hg^{2+})_D$ (ng/L)	$(MMHg)_D$ (ng/L)	$(DMHg)_D$ (ng/L)	$(HgCl_3^-$ *and* $HgCl_4^{2-})_D$ (ng/L)	$(Hg_T)_D$ (ng/L)	$(Hg_T)_P$ (µg/g)	$(Hg_T)_P$ (ng/L)	Hg_T[a] (ng/L)	$log(K_d)$
Dalian	5.49	38.0	0.85	3.95	0.86	0.019	13.26	27.8	0.014	11.9	39.7	2.70
Yingkou	5.58	35.5	4.33	3.81	0.78	0.056	8.97	29.6	0.063	272.8	302.4	3.33
Huludao	5.36	36.0	1.58	3.58	2.36	0.097	11.28	41.1	0.027	42.66	83.76	2.82
Beidaihe	5.01	39.0	0.53	2.00	2.55	0.067	13.65	25.3	0.012	6.36	31.66	2.68
Tianjin	5.63	28.6	5.85	8.90	0.57	n.d.	9.53	35.5	0.051	298.35	333.85	3.16
Yantai	5.97	31.6	5.05	6.19	0.28	0.021	14.12	32.0	0.057	287.85	319.85	3.25
Qingdao	6.12	29.1	5.30	2.17	0.23	n.d.	18.24	32.6	0.044	233.2	265.80	3.13
Xiamen	5.72	34.1	4.66	8.39	0.49	0.136	16.32	30.4	0.039	181.74	212.14	3.11
Guangzhou	5.75	24.7	6.05	2.84	0.40	0.014	12.45	38.0	0.046	278.3	316.30	3.08

[a] $Hg_T = (Hg_T)_D + (Hg_T)_P$.

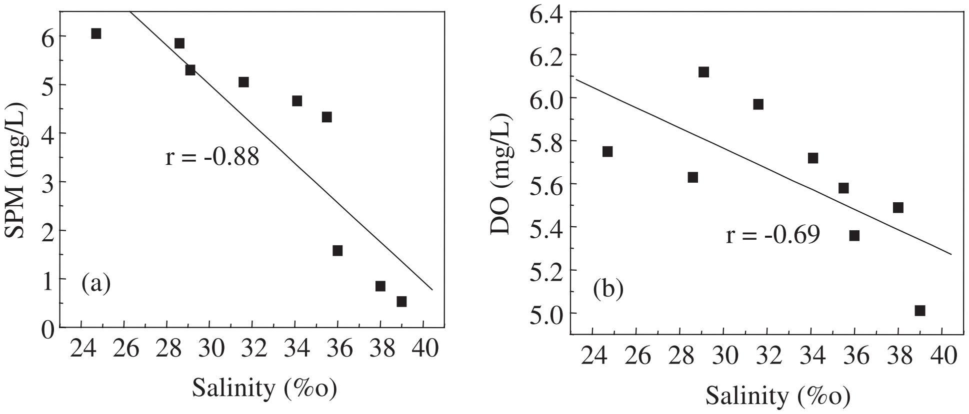

FIGURE 3 Relationship between (a) SPM concentration and salinity, and (b) DO concentration and salinity.

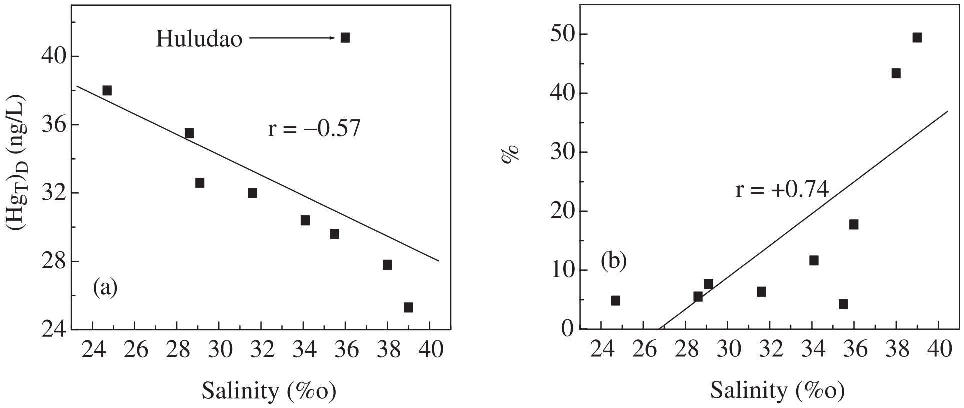

FIGURE 4 Relationship between (a) $(Hg_T)_D$ concentration and salinity, and (b) salinity and the fraction of $(Hg_{Inorg})_D$ in total mercury (Hg_T).

(~35‰ salinity, pH 7.5–8.4), mercuric chlorocomplexes exist primarily as $HgCl_3^-$ and $HgCl_4^{2-}$ [31] due to the average concentration of 0.56 mol/L of Cl^-.

In surface waters of the equatorial Pacific Ocean, Manson and Fitzgerald [7,9] found $(Hg_R)_D$ concentrations of 0.029–0.401 ng/L. For the North Sea, Coquery and Cossa [10] reported $(Hg_R)_D$ concentrations of 0.08–0.36 ng/L. Cossa and Noel [16] also found a low $(Hg_R)_D$ concentration of 0.42 ± 0.14 ng/L. A much higher concentration of inorganic mercury (0.2 μg/L) was found in the Spanish coastal region (Gijon) of the Cantabric Sea [12].

Concentrations and Distribution of Dissolved Monomethylmercury and Dimethylmercury

The concentrations of $(MMHg)_D$ were higher in coastal waters sampled in Beidaihe (2.55 ng/L) and Huludao (2.36 ng/L) than those obtained in other water samples ranging from 0.23 to 0.86 ng/L. Similar concentrations of MMHg were measured in the Scheldt estuary, with concentrations ranging from 0.08 to 0.40 ng/L [18] and from 0.08 to 0.60 ng/L (MMHg concentrations detected in this estuary increased with increased organic matter content and anoxic conditions) [17] and in the Adour estuary from below the detection limit to 0.919 ± 0.035 ng/L [19].

In surface waters of the equatorial Pacific Ocean, $(\mathrm{MMHg})_\mathrm{D}$ was found to range from below the detection limit to 0.06 ng/L [7–9]. Pongratz and Heumann [11] determined the concentration profiles of $(\mathrm{MMHg})_\mathrm{D}$ in surface waters of polar and other remote oceans. In the Atlantic Ocean, the concentrations of $(\mathrm{MMHg})_\mathrm{D}$ ranged from 0.1 to 3 ng/L. The concentration of $(\mathrm{MMHg})_\mathrm{D}$ was even lower in remote areas, and ranged from <0.005 to 0.15 ng/L. In the Polar Oceans, the Antarctic Ocean had 0–0.03 ng/L $(\mathrm{MMHg})_\mathrm{D}$, while the concentrations of $(\mathrm{MMHg})_\mathrm{D}$ ranged from 0 to 0.16 ng/L in the Arctic Ocean.

A significant inverse correlation between $(\mathrm{MMHg})_\mathrm{D}$ concentration and DO content was observed ($r = -0.88$, $P < 0.01$; Fig. 5). Biological methylation in low-oxygen environment is likely to be the most significant process [7]. Concentrations of $(\mathrm{MMHg})_\mathrm{D}$ have a negative correlation with both $(\mathrm{Hg_{Inorg}})_\mathrm{D}$ ($r = -0.48$, $P = 0.19$) and $(\mathrm{Hg_T})_\mathrm{P}$ ($r = -0.67$, $P < 0.05$) concentrations. Meanwhile, the contents of DO were positively correlated with the concentrations of $(\mathrm{Hg_{Inorg}})_\mathrm{D}$ ($r = +0.51$, $P = 0.15$) and $(\mathrm{Hg_T})_\mathrm{P}$ ($r = +0.61$, $P < 0.05$). From the above relationships, we suggest that a low-oxygen environment is conducive to the formation of alkylmercury, labile inorganic mercury is the most probable substrate for methylation [7,9,18], and the supply of particulate mercury provided more mercury for methylation [9]. The relationship between the concentrations of $(\mathrm{MMHg})_\mathrm{D}$ and SPM was significantly negative ($r = -0.81$, $P < 0.01$). A similar pattern was also found by Mason and Fitzgerald [7–9]. Dissolved MMHg can be scavenged by the SPM from the surface seawater.

It has been reported that the amount of MMHg in seawater is only about 1% of the total mercury present [32,33]. Most of the results obtained were below 1% of the total mercury, ranging from 0.09 to 0.26%, but in surface seawater samples from Beidaihe, Huludao and Dalian, the concentrations of $(\mathrm{MMHg})_\mathrm{D}$ were about 8.05, 2.82 and 2.17% of the total mercury, respectively.

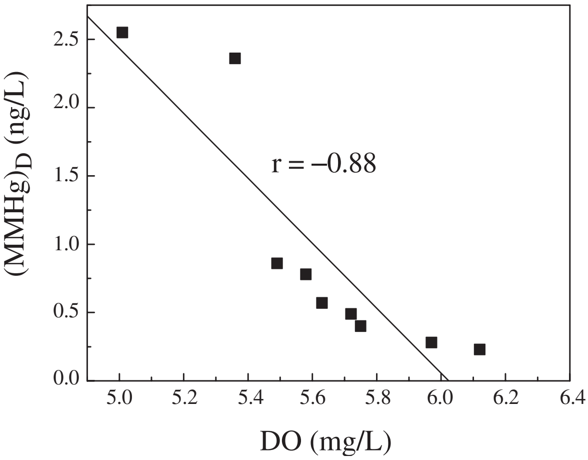

FIGURE 5 Relationship between the concentration of $(\mathrm{MMHg})_\mathrm{D}$ and the dissolved oxygen content.

Dimethylmercury is a volatile mercury species that is liable to exchange between the atmosphere and the surface seawater. The data of $(DMHg)_D$ concentrations in surface waters have been scarcely reported. Mason *et al.* [7,9] found the concentrations of DMHg to range from below the detection limit to 0.154 ng/L in the surface waters of the equatorial Pacific Ocean, whereas in the sub-thermocline waters, the concentrations of DMHg varied between 0.033 ± 0.017 and 0.111 ± 0.031 ng/L [8]. In our study, dissolved DMHg cannot be detected in waters sampled in Qingdao and Tianjin. Although, in other coastal surface water samples, dissolved DMHg was detected, the data were generally below the detection limit (0.126 ng/L), excluding what had been found in the Xiamen water sample. The high concentration of $(DMHg)_D$ (0.136 ng/L), found in the water sample from Xiamen, may be influenced by the phytoplankton blooms of the coastal water.

Concentrations and Distribution of Particulate Mercury

In the transport of Hg^{2+} and MMHg in aquatic systems, particulate transport is more important in particle-rich coastal waters than in the open sea. In our survey, the concentrations of total particulate mercury $[(Hg_T)_P]$ varied between 6.36 and 298.35 ng/L. $(Hg_T)_P$ decreased linearly with the increase in salinity ($r = -0.79$, $P < 0.05$). Also, a linear relationship was observed between $(Hg_T)_P$ and SPM concentrations ($r = +0.90$, $P < 0.01$). Particulate mercury mostly represented 51–90% of all mercury species (dissolved + particulate). From this result, we can see that mercury is predominantly associated with particulate material in coastal waters enriched with SPM. Our result is not significantly different from what had been found in the North Sea (13–82%) [10]. In the Elbe estuary [10], the concentration of $(Hg_T)_P$ ranged from 1.58 to 99.39 ng/L. Compared with a previous study [29], in which the concentrations of total particulate mercury varied between 0.009 and 4.25 μg/L, our data were lower. The much lower level of $(Hg_T)_P$ (0.012 ng/L) was measured in the surface water of the equatorial Pacific Ocean [7].

The total mercury content of the particles from this study varied between 0.012 μg/g and 0.063 μg/g, and the variations were also inversely related to salinity ($r = -0.61$, $P < 0.1$) and positively correlated with the concentrations of SPM ($r = +0.86$, $P < 0.01$). This suggests that particulate mercury was originated from the continent mainly through river inputs. The mercury content of SPM can vary not only with the composition of SPM (e.g. mineral *vs.* biogenic particles), but also with the source of the suspended particulate material [10]. Our data are significantly lower than that for the North Sea (0.116–0.484 μg/g) [10]. The total mercury content of the particles was often high in the estuary, for example, the Scheldt estuary (0.35–1.61 μg/g [17] 0.4–1.7 μg/g [18]) and the Elbe estuary [10] (0.30–1.42 μg/g).

The distribution of Hg between solution and particles is determined by its concentrations in the dissolved and in particulate phase, and the concentration of SPM. The partition of Hg between particulate and dissolved phases is expressed by a dimensionless distribution coefficient, K_d, the ratio of the Hg concentration per unit mass of particulate matter to the dissolved Hg concentration per unit mass (or volume) of seawater [34,35]. In the present study, $\log(K_d)$ ranged between 2.68 and 3.33 (Table III), and the enrichment ability of SPM for dissolved mercury was calculated as 0.5×10^3 to 2.1×10^3. These results are lower than those reported by Coquery and Cossa [10] for the North Sea [$\log(K_d)$ between 5.09 and 6.04]. We observed a trend of increasing

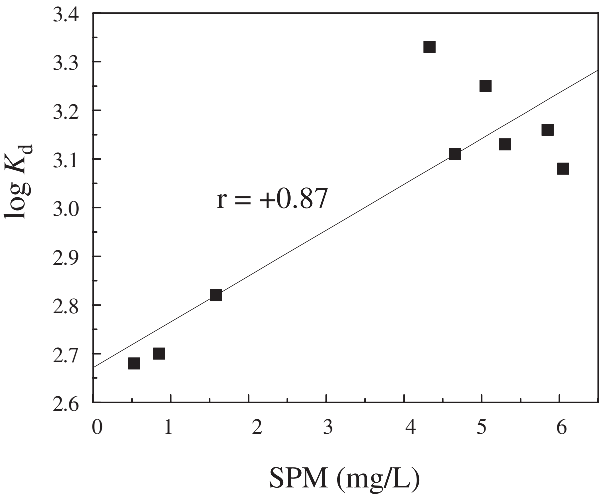

FIGURE 6 Relationship between log(K_d) and the content of suspended particulate matter.

log(K_d) with increasing SPM concentration ($r = +0.87$, $P < 0.01$; Fig. 6). This trend is in contrast to that found by Coquery and Cossa [10] and Balls [34]. In their studies, the 0.8-μm quartz fiber filters were used, and not all colloidal matter (submicron-sized particles) was collected. Their operationally defined 'dissolved' fraction was likely to include Hg species that were associated with colloids plus truly dissolved mercury. The observed increase in $(Hg_T)_D$ concentrations with SPM probably results from the association of a fraction of the 'apparently dissolved' Hg with colloidal particles, which are more abundant at high SPM concentrations. However, in our research work, we used the 0.45-μm Millipore cellulose membrane, and so the above-mentioned analytical artifact was reduced to some extent. The concentrations of $(Hg_T)_D$ measured in the present study have no significant correlation with the concentrations of SPM ($r = +0.38$, $P = 0.32$), whereas $(Hg_T)_P$ increased greatly with the increase in SPM ($r = +0.86$, $P < 0.01$). Therefore, a positive relationship was obtained between log(K_d) and SPM concentrations.

CONCLUSION

The present study has outlined methodologies for the determination of $(Hg_T)_D$, $(Hg_T)_P$, $(MMHg)_D$ and $(DMHg)_D$, particularly, $(Hg^{2+})_D$ and $(HgCl_3^-$ and $HgCl_4^{2-})_D$. The analysis methods are satisfactorily reliable, and TCF adsorbent provides effective preconcentration for the determination of trace levels of Hg^{2+} and MMHg in seawater. A survey of mercury speciation distribution in surface seawater sampled from nine coastal cities in China was carried out.

The concentration of $(Hg_T)_D$ in Huludao surface seawater is highest due to considerable industrial blow-off. The Xiamen seawater sample showed the highest $(DMHg)_D$ concentration. Higher levels of $(MMHg)_D$ were found in surface seawaters sampled in Beidaihe, Huludao and Dalian. The correlations between $(MMHg)_D$ concentration and DO, $(Hg_{Inorg})_D$, $(Hg_T)_P$ content validate the views that the low-oxygen environment is conducive to the formation of methylmercury species, labile inorganic mercury is the most probable substrate for methylation, and the supply of particulate mercury provides more mercury for methylation. Using a 0.45-μm Millipore cellulose membrane, a positive relationship between log(K_d) and the SPM concentrations was found. Compared with previous monitoring reports in China, it can be seen that mercury pollution in surface seawater was reduced during the last decades. However, mercury pollution is still an environmental problem in China compared with mercury levels in other harbors, estuaries, and oceans of the world.

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References

[1] A. Boudou and F. Ribeyre, *Water Air Soil Pollut.*, **26**, 137–148 (1985).
[2] L. Friberg, G.F. Nordberg and V.B. Vouk, In: *Handbook on the Toxicology of Metals*, Vol. II. Elsevier Science, Amsterdam (1986).
[3] G. Westöö, *Science*, **181**, 567–568 (1973).
[4] R. Kiyoura, In: E.A. Pearson (Ed.) *Advances in Water Pollution Research*. Pergamon Press, New York (1964).
[5] A.G. Johnels and T. Westermark, In: M.W. Miller and G.G. Berg (Eds.) *Chemical Fallout*. Thomas CC, Springfield, IL (1969).
[6] M. Morita, J. Yoshinaga and J.S. Edmonds, *Pure Appl. Chem.*, **70**, 1585–1615 (1998).
[7] R.P. Mason and W.F. Fitzgerald, *Nature*, **374**, 457–459 (1990).
[8] R.P. Mason and W.F. Fitzgerald, *Water Air Soil Pollut.*, **56**, 779–789 (1991).
[9] R.P. Mason and W.F. Fitzgerald, *Deep-Sea Res. I*, **40**, 1897–1924 (1993).
[10] M. Coquery and D. Cossa, *Neth. J. Sea Res.*, **34**, 245–257 (1995).
[11] R. Pongratz and K.G. Heumann, *Int. J. Environ. Anal. Chem.*, **71**, 41–56 (1998).
[12] B. Aizpún, M.L. Fernández, E. Blanco and A. Sanz-Medel, *J. Anal. Atom. Spectrosc.*, **9**, 1279–1284 (1994).
[13] Ph. Quevauviller, K.J.M. Kramer, E.M. Van der Vlies, W. Dorten and B. Griepink, *Fresenius' J. Anal. Chem.*, **356**, 411–415 (1996).
[14] M.J. Bloxham, A. Gachanja, S.J. Hill and P.J. Worsfold, *J. Anal. Atom. Spectrosc.*, **11**, 145–148 (1996).
[15] M.J. Bloxham, S.J. Hill and P.J. Worsfold, *J. Anal. Atomic Spectrosc.*, **11**, 511–514 (1996).
[16] D. Cossa and J. Noel, *Mar. Chem.*, **20**, 389–396 (1987).
[17] W. Baeyens, C. Meuleman, B. Muhaya and M. Leermakers, *Hydrobiologia*, **366**, 63–79 (1997–1998).
[18] M. Leermakers, C. Meuleman and W. Baeyens, *Water Air Soil Pollut.*, **80**, 641–652 (1995).
[19] T. Stoichev, R.C. Rodriguez Martin-Doimeadios, D. Amouroux, N. Molenat and O.F.X. Donard, *J. Environ. Monit.*, **4**, 517–521 (2002).
[20] Y.H. Lee, *Int. J. Environ. Anal. Chem.*, **29**, 263–276 (1987).
[21] Y.H. Lee and J. Mowrer, *Anal. Chim. Acta*, **221**, 259–268 (1989).
[22] M.L. Mena, C.W. Mcleod, P. Jones, A. Withers, V. Minganti, R. Capelli and P. Quevallviller, *Fresenius' J. Anal. Chem.*, **351**, 456–460 (1995).
[23] J. Wei and C.W. Mcleod, *Talanta*, **39**, 1537–1542 (1992).
[24] E. Schulek and K. Burger, *Talanta*, **1**, 219–223 (1958).
[25] N.S. Bloom and E.A. Crecelius, *Mar. Chem.*, **14**, 49–59 (1983).
[26] J.D. Burton and T.M. Leatherland, *Nature*, **231**, 440–442 (1971).
[27] M.Q. Yu, W. Tian, D.W. Sun, W.B. Shen, G.P. Wang and N. Xu, *Anal. Chim. Acta*, **428**, 209–218 (2001).
[28] B. Wen, X.Q. Shan and S.G. Xu, *Analyst*, **124**, 621–626 (1999).
[29] *Records of China Bay*. The Compilation Council for 'Records of China Bay'. Ocean Press, Beijing (1993).
[30] H.K. Gu, *Marine Chemistry of the Bohai Sea, the Yellow Sea and the East China Sea*. Science Press, Beijing (1991).

[31] S.M. Ullrich, T.W. Tanton and S.A. Abdrashitova, *Crit. Rev. Environ. Sci. Technol.*, **3**, 241–293 (2001).
[32] J. Yamamoto, Y. Kaneda and Y. Hikasa, *Int. J. Environ. Anal. Chem.*, **16**, 1–16 (1983).
[33] M. Horvat, S. Covelli, J. Faganeli, M. Logar, V. Mandić, R. Rajar, A. Širca and D. Žagar, *Sci. Total Environ.*, **237–238**, 43–56 (1999).
[34] P.W. Balls, *Neth. J. Sea Res.*, **23**, 7–14 (1989).
[35] J.D. Burton, M. Althaus, G.E. Millward, A.W. Morris, P.J. Statham, A.D. Tappin and A. Turner, *Phil. Trans. R. Soc. Lond.* A, **343**, 557–568 (1993).