

## Simultaneous observations of ammonia in the atmosphere and ocean

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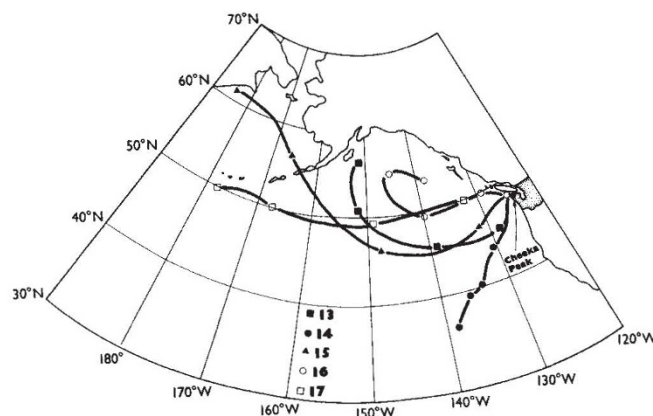


Fig. 1 Study area along the coast of Washington State. Samples were collected from the NOAA ship *McArthur* (5–200 km from shore) and on top of Cheeka Peak at the northernmost tip of Washington State. Also shown are the calculated four-day isentropic air mass trajectories\* for 13–17 May 1987.

Ammonia, being the dominant base other than sea salt in the remote marine troposphere, plays an important role in the acid-base chemistry of the atmosphere<sup>1–3</sup>. An understanding of the cycling of ammonia through the marine environment has, until now, been hampered by the lack of concurrent measurements of key acidic and basic atmospheric and seawater species. Reported here are the results of simultaneous concentration measurements of these species during May 1987 in the coastal north-east Pacific Ocean environment. Gas (g) and particulate (p) phase data suggest that low concentrations of  $\text{NH}_3$  (g) in the marine atmosphere lead to partly neutralized  $\text{H}_2\text{SO}_4$  in aerosol particles and in rainwater. Gas-phase concentrations combined with seawater concentration measurements indicate that for the region and time period studied the ocean was a local source of atmospheric ammonia. These data, combined in a simple box model, suggest a marine boundary layer residence time of 3.6 h and 22 h for  $\text{NH}_3$  (g) and  $\text{NH}_4^+$  (p), respectively.

Samples were collected from 8 to 22 May 1987 at the coastal mountaintop site on Cheeka Peak (48°18' N; 124°37' W; altitude 480 m) on the northernmost tip of Washington state and aboard the NOAA ship, *McArthur*, in the coastal waters of the north-east Pacific Ocean (Fig. 1). During this period the biological productivity in the surface ocean waters was seasonably high with primary productivity rates of 12 to 450  $\text{mg C m}^{-3} \text{ d}^{-1}$ . The phytoplankton standing stock, as measured by chlorophyll 'a', ranged from 1 to 15  $\text{mg m}^{-3}$ . The species sampled were atmospheric gas phase ammonia,  $\text{NH}_3$  (g), atmospheric particulate phase ammonium and non-seasalt sulphate,  $\text{NH}_4^+$  (p) and n.s.s.  $\text{SO}_4^{2-}$  (p) respectively, dissolved unionized and ionized ammonia in sea water,  $\text{NH}_3$  (s) and  $\text{NH}_4^+$  (s), and  $\text{NH}_3$  in equilibrium with sea water.

Atmospheric samples were collected 7 m above the land surface at Cheeka Peak. The shipboard samples were collected from a boom extending 6 m upwind of the ship and 10 m above the sea surface. Samples were taken only during periods of SW to NW on-shore winds and when the total particle (CN) count was less than 1,000  $\text{cm}^{-3}$ . This procedure coupled with the use of calculated air mass trajectories<sup>4</sup> (Fig. 1), ensured the sampling of purely remote marine air.

A tandem sampling system was used which consisted of a cyclone separator (50 per cent collection efficiency at 0.9  $\mu\text{m}$  for NaCl particles) followed by a 47-mm Millipore Teflon filter (1.0- $\mu\text{m}$  pore size) for the collection of particulate species and four oxalic-acid-impregnated Whatman 41 filters for the collection of  $\text{NH}_3$  (g). The cyclone fraction was discarded. The four Whatman filters were used in series to ensure a high collection efficiency for  $\text{NH}_3$  (g). Laboratory tests have shown the  $\text{NH}_3$  (g) collection efficiency of this system to be nearly 100% (P. K. Quinn and T. S. Bates, manuscript in preparation). A second stacked filter pack was mounted alongside each sample to serve as a sampling and analytical blank (sample flow rate was 52 standard  $\text{l m}^{-1}$  while blank flow rate was 0 standard  $\text{l m}^{-1}$ ). The  $\text{NH}_4^+$  (p) blank concentration was typically below the detection limit of 0.1  $\mu\text{mol l}^{-1}$ , the mean n.s.s.  $\text{SO}_4^{2-}$  (p) blank concentra-

tion was 11% of the sample concentration and the mean  $\text{NH}_3$  (g) blank concentration was 30% of the sample concentration.

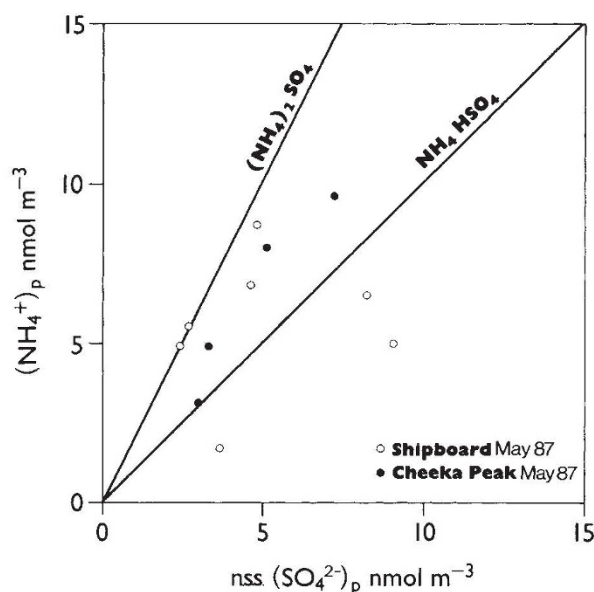
Bulk seawater samples were taken from a depth of 5 m for the determination of the  $\text{NH}_4^+$  (s) +  $\text{NH}_3$  (s) concentration. An equilibrator, consisting of a closed volume of air in contact with a large volume of continually replenished sea water<sup>5</sup>, was used to measure the saturation concentration of ammonia,  $(\text{NH}_3)_{\text{sg}}$ , relative to its concentration in ocean surface waters. Measurements of  $[\text{NH}_4^+] + [\text{NH}_3]_{\text{s}}$  and  $(\text{NH}_3)_{\text{sg}}$  showed that the equilibrator functioned within a factor of three of Henry's Law. (Round brackets indicate concentrations in the atmosphere, that is, in the gas and particle phases. Square brackets indicate concentrations in the liquid phase, that is, in sea water and rainwater.) But this calculation was based on a measured Henry's Law constant<sup>6</sup>,  $K_{\text{hN}}$ , for a low ionic strength solution measured at 25 °C and corrected to the equilibrator sea water temperature of 11 °C. A measured  $K_{\text{hN}}$  for  $\text{NH}_3$  in sea water at the appropriate temperature would improve these calculations. The  $\text{NH}_3$  blank concentration for this system (equilibrator tubing, pump and filter pack, excluding the sea water) was typically 20% of the sample value. The bulk seawater samples were taken from the same line that served as the sea water supply for the equilibrator.

The phenolphthorite colorimetric technique<sup>7</sup> was used for all ammonia analyses. Ion chromatography was used for the  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  determinations. All ammonia samples were analysed within 6 h of collection while the  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  filter samples were extracted with methanol and water and frozen for later analysis. All sample handling was carried out in an  $\text{NH}_3$  and  $\text{SO}_2$  free glove box, both in the laboratory and field.

The mean and sample standard deviation of the measured shipboard and Cheeka Peak  $(\text{NH}_3)_{\text{g}}$  were  $1.3 \pm 0.7 \text{ nmol m}^{-3}$  (number of samples  $n = 14$ ) and  $0.76 \pm 0.35 \text{ nmol m}^{-3}$  ( $n = 8$ ), respectively, with an average difference between duplicate samples of 41%. The range of concentrations measured here encompasses the mean value of 3.5  $\text{nmol m}^{-3}$  measured in maritime air at Cape Grim (40°41' S; 144°41' E) (ref. 8). The shipboard and Cheeka Peak concentrations of  $\text{NH}_4^+$  (p) were  $5.9 \pm 2.4 \text{ nmol m}^{-3}$  ( $n = 13$ ) and  $6.1 \pm 3.2 \text{ nmol m}^{-3}$  ( $n = 8$ ), respectively, with an average difference between duplicate samples of 33%. These values fall within the range of  $(\text{NH}_4^+)_{\text{p}}$ , 0.5–15  $\text{nmol m}^{-3}$ , found over the Pacific Ocean by Parungo *et al.*<sup>9</sup>. Non-seasalt  $(\text{SO}_4^{2-})_{\text{p}}$  were calculated from measured  $(\text{Na}^+)_{\text{p}}$ . The shipboard and Cheeka Peak n.s.s.  $(\text{SO}_4^{2-})_{\text{p}}$  were  $5.1 \pm 2.6 \text{ nmol m}^{-3}$  ( $n = 7$ ) and  $4.6 \pm 2.0 \text{ nmol m}^{-3}$  ( $n = 4$ ), respectively. The seasalt  $(\text{SO}_4^{2-})_{\text{p}}$  was always less than 8% of the total  $(\text{SO}_4^{2-})_{\text{p}}$ .

The  $\text{NH}_4^+$  (p) to n.s.s.  $\text{SO}_4^{2-}$  (p) molar ratio measured on the ship was  $1.3 \pm 0.7$  while that at Cheeka Peak was  $1.3 \pm 0.3$  (Fig. 2).





**Fig. 2** Particulate n.s.s.  $(\text{SO}_4^{2-})_p$  versus  $(\text{NH}_4^+)_p$  for air masses over the NE Pacific Ocean during May 1987. Shipboard and Cheeka Peak samples have a correlation coefficient of 0.83 and 0.89, respectively. Samples falling on the line marked  $(\text{NH}_4)_2\text{SO}_4$  have an  $\text{NH}_4^+(p)$  to n.s.s.  $\text{SO}_4^{2-}(p)$  molar ratio of 2 while those on the line marked  $\text{NH}_4\text{HSO}_4$  have a ratio of 1.

Fully neutralized  $\text{H}_2\text{SO}_4$  aerosol particles would have an  $\text{NH}_4^+(p)$  to n.s.s.  $\text{SO}_4^{2-}(p)$  molar ratio of 2. The measured molar ratio suggests a mean particulate chemical composition between  $\text{NH}_4\text{HSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  and is consistent with the  $\text{NH}_4^+(r)$  to n.s.s.  $\text{SO}_4^{2-}(r)$  molar ratio of  $\sim 1$  found in remote marine rain<sup>2,10</sup>. On the basis of these data, it appears that the low availability of  $\text{NH}_3(g)$  in remote marine air leads to partially neutralized  $\text{H}_2\text{SO}_4$  particulates. Since some of the partly neutralized  $\text{H}_2\text{SO}_4$  aerosol particles act as cloud condensation nuclei<sup>11</sup> and are the main source of n.s.s.  $\text{SO}_4^{2-}$  in remote marine rainwater, low  $\text{NH}_3(g)$  concentrations yield rainwater that is only 30–60% neutralized<sup>12</sup>.

The flux of a gas-phase rate-controlled gas into or out of the ocean surface can be described by

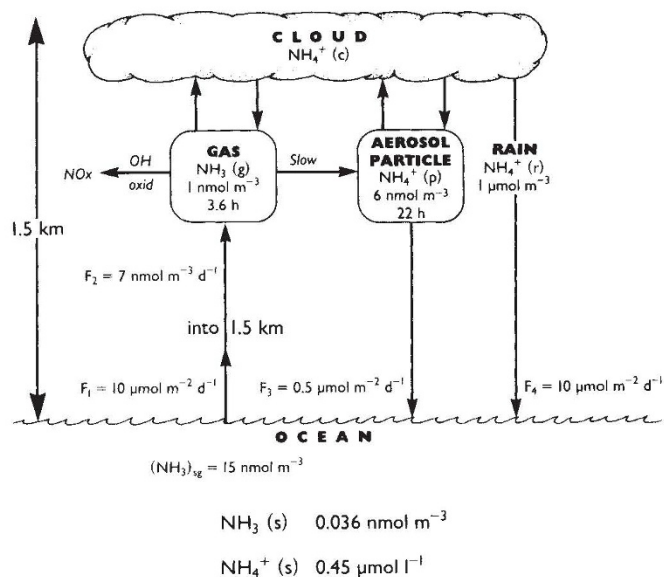
$$F = k_g(c_{sg} - c_g) \quad (1)$$

where  $F$  is the flux,  $k_g$  is the gas phase transport coefficient of the gas,  $c_{sg}$  is the saturation concentration of the gas relative to its concentration in the surface ocean waters, and  $c_g$  is the bulk atmospheric gas concentration<sup>13</sup>. For ammonia,  $c_g$  is  $(\text{NH}_3)_g$  and  $c_{sg}$  is  $(\text{NH}_3)_{sg}$  and is related to  $[\text{NH}_3]_s$ , the dissolved unionized form of the gas in the ocean, through Henry's Law. This relation is given by

$$K_{hN} = (\text{NH}_3)_{sg} / [\text{NH}_3]_s \quad (2)$$

To date, all seawater measurements of ammonia species have yielded only the sum of the  $\text{NH}_4^+(s)$  and  $\text{NH}_3(s)$  concentrations. Since  $\text{NH}_3(s)$  is the active species in the air/sea exchange of ammonia, it is necessary to know its saturation concentration relative to its concentration in ocean surface waters to obtain an accurate estimate of the flux of ammonia into or out of the ocean.

Bulk seawater, equilibrator, and gas phase atmospheric samples were collected simultaneously for analysis of  $[\text{NH}_4^+]_s + [\text{NH}_3]_s$ ,  $(\text{NH}_3)_{sg}$  and  $(\text{NH}_3)_g$ , respectively. The bulk seawater  $([\text{NH}_4^+]_s + [\text{NH}_3]_s)$  was  $0.45 \pm 0.35 \mu\text{mol l}^{-1}$  ( $n = 48$ ).  $(\text{NH}_3)_{sg}$  ranged from 4.9 to 22  $\text{nmol m}^{-3}$  with a mean of  $16 \pm 7.1$  ( $n = 6$ ) while  $(\text{NH}_3)_g$  ranged from 0.81 to 1.4  $\text{nmol m}^{-3}$  with a mean of  $0.97 \pm 0.27$  ( $n = 10$ ).



**Fig. 3** Box model for ammonia species in the remote marine environment over the NE Pacific Ocean during May 1987. The average box height (1.5 km) was determined from radiosonde measurements. All concentrations were measured simultaneously.  $F_1 = k_g(c_{sg} - c_g) = 10 \mu\text{mol m}^{-2} \text{d}^{-1}$ . This flux of  $\text{NH}_3(g)$  into a height of 1.5 km corresponds to an input rate  $F_2$  of  $7 \text{ nmol m}^{-3} \text{d}^{-1}$ .  $F_3$  is the dry deposition flux of  $\text{NH}_4^+(p)$  using the given concentration of  $\text{NH}_4^+(p)$  and a deposition velocity of  $0.1 \text{ cm s}^{-1}$ , which corresponds to a particle radius  $< 0.5 \mu\text{m}$ .  $F_4$  is based on the given rainwater concentration, a total rainfall amount of 2.0 cm, and the time since the last rainfall, 2 days. The lifetimes of  $\text{NH}_3(g)$  and  $\text{NH}_4^+(p)$ ,  $t_1$  and  $t_2$  respectively, are calculated from the given concentrations and the value of  $F_2$ .

$(\text{NH}_3)_{sg}$  were consistently an order of magnitude higher than  $(\text{NH}_3)_g$  which, by use of equation (1), suggests that for the region studied the ocean was a net source of ammonia. The flux of ammonia out of the ocean calculated via equation (1) was found to range between 2.6 and  $16 \mu\text{mol m}^{-2} \text{d}^{-1}$  with a mean of  $10 \pm 5$  ( $n = 6$ ). The transport coefficient used was that of  $\text{H}_2\text{O}$ ,  $3,000 \text{ cm h}^{-1}$ , as both  $\text{H}_2\text{O}$  and  $\text{NH}_3$  are gas-phase rate-controlled species and have similar molecular weights<sup>13</sup>. An empirically determined  $k_g$  for  $\text{NH}_3$  would improve the accuracy of these calculations.

The flux derived from the measured  $(\text{NH}_3)_{sg}$  and  $(\text{NH}_3)_g$  values was compared to one calculated from bulk seawater measurements of  $[\text{NH}_3]_s + [\text{NH}_4^+]_s$  as described by Ayers and Gras<sup>8</sup>. Based on the  $([\text{NH}_3]_s + [\text{NH}_4^+]_s)$ ,  $F$  was calculated to be  $3.1 \mu\text{mol m}^{-2} \text{d}^{-1}$ . Although this flux is within the range of values calculated using the equilibrator values of  $(\text{NH}_3)_{sg}$ , it is a factor of three lower than the calculated mean flux of  $10 \mu\text{mol m}^{-2} \text{d}^{-1}$ . At least one difficulty in using  $([\text{NH}_3]_s + [\text{NH}_4^+]_s)$  for the determination of  $(\text{NH}_3)_{sg}$  is the lack of a measured  $K_{hN}$  for  $\text{NH}_3$  in sea water. The equilibrator technique does not require the use of  $K_{hN}$ . Although it has not been used previously for  $\text{NH}_3$  measurements it has been shown to work well with other gases ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{DMS}$ ) (ref. 5 and J. E. Johnson, unpublished data).

The  $\text{NH}_3(g)$ ,  $\text{NH}_4^+(p)$ ,  $\text{NH}_4^+(s)$  and  $\text{NH}_3(s)$  data are compared in a box model in Fig. 3.  $\text{NH}_3$  is released from the ocean to the atmosphere with an average flux  $F_1 = 10 \mu\text{mol m}^{-2} \text{d}^{-1}$ . An average height of the well mixed marine boundary layer during this study, as determined from radiosonde measurements, was  $\sim 1.5 \text{ km}$ . The flux of  $10 \mu\text{mol m}^{-2} \text{d}^{-1}$  corresponds to an input rate into this height,  $F_2$ , of  $7 \text{ nmol m}^{-3} \text{d}^{-1}$ . The  $\text{NH}_3(g)$  concentration measured in this study was  $\sim 1 \text{ nmol m}^{-3}$ . The majority of the  $\text{NH}_3(g)$  reacts with  $\text{H}_2\text{SO}_4$  aerosol particles or



is dissolved into cloud droplets. Since these two processes occur much faster than the reaction of  $\text{NH}_3$  (g) with OH radical, only a small portion of the  $\text{NH}_3$  is oxidized<sup>14-16</sup>. The measured average  $\text{NH}_4^+$  (p) concentration in the remote marine troposphere was  $6 \text{ nmol m}^{-3}$ . There are no reported measurements to date of  $\text{NH}_4^+$  in remote marine cloudwater.

Turnover times of  $t_1 = 3.6 \text{ h}$  and  $t_2 = 22 \text{ h}$  for  $\text{NH}_3$  (g) and  $\text{NH}_4^+$  (p), respectively, were calculated from average concentrations and  $F_2$ . The short turnover time for  $\text{NH}_3$  (g) reflects its rapid accretion onto the condensed phase during passage through a cloud and its subsequent inability to return to the gas phase after the cloud droplet evaporates. The time of  $3.6 \text{ h}$  is consistent with vertical mixing times of the marine planetary boundary layer<sup>14</sup>.

A dry deposition flux for  $\text{NH}_4^+$  (p) ( $F_3$ ) of  $0.5 \mu\text{mol m}^{-2} \text{ d}^{-1}$  was calculated using the average  $(\text{NH}_4^+)_p$  and a deposition velocity of  $0.1 \text{ cm s}^{-1}$  which corresponds to a particle radius of less than  $0.5 \mu\text{m}$ . The rainwater concentration of  $\text{NH}_4^+$  was  $1.0 \pm 0.1 \mu\text{mol l}^{-1}$  during one storm sampled aboard the ship *McArthur* on 13 May 1987. Based on a total rainfall amount of  $2.0 \text{ cm}$  and the time since the previous rainfall (two days), the wet depositional flux ( $F_4$ ) was  $10 \mu\text{mol m}^{-2} \text{ d}^{-1}$ . This rainwater flux is consistent with the range of  $2$  to  $14 \mu\text{mol m}^{-2} \text{ d}^{-1}$  measured over the Pacific Ocean<sup>2</sup> by Galloway. The agreement of the wet deposition flux of  $\text{NH}_4^+$ ,  $F_4$ , with the measured flux out of the ocean,  $F_1$ , ( $10 \mu\text{mol m}^{-2} \text{ d}^{-1}$ ) indicates that  $\text{NH}_3$  is conserved as it cycles through the marine environment.

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## Origin of technetium-99 and its use as a marine tracer

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The Chernobyl accident caused a variety of radionuclides to be released. The most abundant of the longer-lived nuclides were the two caesium isotopes  $^{137}\text{Cs}$  and  $^{134}\text{Cs}$ , with half lives of 30 yr and 2.06 yr respectively<sup>1</sup>. For many years<sup>2-5</sup> these radionuclides have been used as oceanographic tracers in the north-east Atlantic Ocean. Their sources are the fuel reprocessing plants in Western Europe. The radiocaesium released from Chernobyl, however, was deposited very inhomogeneously<sup>6</sup>, thus seriously perturbing its use as a tracer. So, there is a need to identify another tracer with the same sources but unperturbed by input from Chernobyl. Technetium-99 is not sedimented to any great degree and thus as a conservative tracer<sup>7</sup> can be considered as a candidate. In a recent study<sup>2</sup> we found the same dilution factor for technetium as for radiocaesium when comparing concentrations in the North Sea with those in coastal waters around Greenland, supporting the idea of technetium as a substitute tracer for radiocaesium. Here we report a study of the possible contributions to  $^{99}\text{Tc}$  in order to determine the Chernobyl input. We chose the Baltic Sea for our study because it probably shows higher concentrations of Chernobyl debris than any other sea. We show that the Chernobyl contribution is such that  $^{99}\text{Tc}$  can be used as a tracer.

There are three possible main contributors to the  $^{99}\text{Tc}$  content of the Baltic Sea; fallout from nuclear weapons testing in the 1950s and 1960s, liquid discharge from nuclear reprocessing in Western Europe and the Chernobyl accident. To test our

hypothesis seawater samples were collected during an FS *Gauss* cruise (arranged by the German Hydrographic Institute) to the Baltic Sea in October-November 1986, which were subsequently analysed for  $^{99}\text{Tc}$ ,  $^{137}\text{Cs}$  and  $^{134}\text{Cs}$ .

From seaweed measurements in earlier years<sup>8</sup>, we know that only very small amounts of  $^{99}\text{Tc}$  have entered the Baltic and we would therefore expect a low background when measuring the Chernobyl contribution of  $^{99}\text{Tc}$ . Thus, if Chernobyl-produced  $^{99}\text{Tc}$  was indeed present in the marine environment, the Baltic Sea would be a likely place to detect it. Moreover, the Baltic is one of the seas most contaminated by Chernobyl fallout<sup>9,10</sup>.

The samples analysed consisted of 200 l of sea water. After collecting,  $^{99\text{m}}\text{Tc}$  yield tracer (metastable form of  $^{99}\text{Tc}$ ) was added to the water on board the ship. The tracer showed that ferrihydroxide precipitation under reducing conditions collected the technetium in nearly 100% yield. Technetium analysis was performed after the radiochemical solvent extraction from the hydroxide precipitate<sup>11</sup>.

Gamma-ray spectra of the plated Tc isolates revealed radionuclides other than  $^{99}\text{Tc}$ , principally  $^{106}\text{Ru}$ ,  $^{103}\text{Ru}$  and  $^{110\text{m}}\text{Ag}$ . Thus the radiochemical procedure used hitherto could not be applied, and it was necessary to develop a new method<sup>12</sup> which could effectively remove these elements. In this method Tc and Ru are oxidized to  $\text{TcO}_4^-$  and  $\text{RuO}_4^-$  by  $\text{NaClO}$  and separated from other radionuclides by extraction with  $\text{CCl}_4$  at  $\text{pH} = 4$ . The ruthenium is reduced to low valence, whereas Tc is maintained as  $\text{TcO}_4^-$  using  $\text{H}_2\text{O}_2$ . Thus separated, Tc, Ru and the other radionuclides are subsequently isolated by solvent extraction with cyclohexanone and 5% triisooctylamine/xylene. Technetium is electroplated onto stainless steel disks. The radiochemical yield is determined by gamma-counting  $^{99\text{m}}\text{Tc}$  prior to low-level beta-counting<sup>11</sup>. The decontamination factor for this method is  $10^5$  for Ru and  $2 \times 10^5$  for Ag. The lower limit of detection for a 200 l seawater sample is  $0.014 \text{ Bq } ^{99}\text{Tc m}^{-3}$ .

Figure 1 shows the distribution of  $^{99}\text{Tc}$  in the Baltic Sea. Samples from the Cattegat contained about  $1-2 \text{ Bq } ^{99}\text{Tc m}^{-3}$ , as expected from earlier studies<sup>13</sup>. In the Baltic Sea the levels drop below  $0.1 \text{ Bq m}^{-3}$ . If the  $^{99}\text{Tc}$  was from Chernobyl we would have expected to find the highest levels in the surface water, as observed for  $^{137}\text{Cs}$ ; instead, the  $^{99}\text{Tc}$  concentrations in the Baltic