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**Field observations of the ocean-atmosphere exchange of ammonia: a comparison of high and low latitudes reveals the fundamental importance of temperature.**

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32 **Abstract.** Simultaneous measurements of  $\text{NH}_3$  in the atmosphere and  $\text{NH}_4^+$  in the ocean are  
33 presented from fieldwork spanning 10 years and 110 degrees of latitude, including the first such  
34 simultaneous measurements in the remote marine environment at  $>55^\circ\text{N}$ . At high latitudes, fluxes  
35 were almost exclusively from air to sea, in contradiction with previous lower latitude studies, which  
36 have suggested that the open oceans are predominantly sources of ammonia to the atmosphere.

37 Sensitivity analysis demonstrates that the direction and magnitude of the sea-air  $\text{NH}_3$  exchange is  
38 highly dependent on water temperature. This temperature effect is sufficiently strong to outweigh  
39 the effects of variability in concentrations in seawater and atmosphere in many parts of the (open)  
40 ocean. This is highlighted in data from the Atlantic oligotrophic gyres, where fluxes were found to  
41 be predominantly out of the ocean despite extremely low dissolved ammonium concentrations in  
42 surface waters.

43 **1. Introduction**

44 Ammonia ( $\text{NH}_3$ ) is important in the biogeochemical cycling and geographic redistribution of  
45 nitrogen and in its potential climate forcing role through its connections to the sulphur cycle and  
46 cloud formation [*Liss and Galloway, 1993*]. In the atmosphere and ocean, ammonia and its  
47 protonated form, ammonium ( $\text{NH}_4^+$ ) are ubiquitous. Naturally and anthropogenically produced  $\text{NH}_x$   
48 ( $\text{NH}_3 + \text{NH}_4^+$ ) is transported through the atmosphere and generally occurs in decreasing  
49 concentration in air with distance from land. It has been suggested that in pre-industrial times the  
50 oceans were probably a net source of  $\text{NH}_x$  to the continents [*Duce et al, 1991*], but this is not the  
51 case today. Generally speaking, seawater  $\text{NH}_x$  concentrations are lower in regions of low  
52 productivity; nutrient-limited communities being more efficient at utilising recycled nitrogen and  
53 thus maintaining a lower ambient concentration. Thus, high latitudes tend to have substantially  
54 greater  $\text{NH}_x$  concentrations than low latitudes in the open ocean, with high productivity coastal and  
55 shelf seas tending to have highest concentrations, irrespective of latitude [*Johnson, 2004*].

56  $\text{NH}_x$  is produced in surface waters by the biological reduction of nitrate (either directly or via the  
57 degradation of biologically synthesised organic nitrogenous material). In solution it is partitioned  
58 between ammonium and ammonia according to equilibrium thermodynamics: the proportion of  
59  $\text{NH}_x$  that occurs as  $\text{NH}_3$  (dependent on pH, temperature and ionic strength of the medium) is  
60 available for emission to the atmosphere; the phase partitioning being dependent on the Henry's  
61 Law coefficient. Ammonia is also emitted to the atmosphere by plants and animals in terrestrial  
62 environments (both directly and through breakdown of organic nitrogen) by soil micro-organisms

63 and by various industrial and agricultural processes, including the direct volatilization of solid  
64 ammonium nitrate salts in fertilizer. There is also evidence of a volcanic source of  $\text{NH}_x$  to the  
65 atmosphere [Uematsu *et al*, 2004], and of substantial ammonia emissions from seabird and seal  
66 colonies [Blackall *et al*, 2007; Theobald *et al*, 2006].

67 Although in most earth-surface environments the aqueous phase partitioning between  $\text{NH}_3$  and  
68  $\text{NH}_4^+$  is dominated by the latter species ( $\text{NH}_3$  only becoming dominant at  $\text{pH} > 9$ -10 under typical  
69 environmental conditions), the majority of emission to the atmosphere from terrestrial and marine  
70 surfaces is as  $\text{NH}_{3(g)}$ . Once in the atmosphere, ammonia reacts readily with acid gases and acidic  
71 aerosols and enters the particulate phase as  $\text{NH}_4^+_{(p)}$ . This is a slight simplification: in aerosol with an  
72 aqueous component a small proportion of the particulate  $\text{NH}_x$  will be in the form  $\text{NH}_3$  (albeit  $\ll 1\%$   
73 in low pH aerosol solutions). However, it is a convenient simplification to consider  $\text{NH}_x$  in the  
74 atmosphere to be partitioned between *gas phase*  $\text{NH}_3$  and *particle phase*  $\text{NH}_4^+$ , which convention  
75 we adopt following previous workers in the field e.g. Gibb *et al*, [1999].

76 Whilst  $\text{NH}_{3(g)}$  can be deposited from the atmosphere by wet deposition processes and direct uptake  
77 onto aqueous surfaces, deposition is dominated by the particulate form [Warneck, 1988], suggesting  
78 net transformation of  $\text{NH}_{3(g)}$  to  $\text{NH}_4^+_{(p)}$ . However, this process is reversible, at least under some  
79 conditions [Milford *et al*, 2000]. It has been suggested that in the remote marine atmosphere (i.e.  
80 away from significant terrestrial influence), gas and particle phases in the atmosphere *and* boundary  
81 layer atmosphere and surface seawater should be at or close to equilibrium with respect to  $\text{NH}_x$   
82 [Quinn *et al*, 1992; Johnson, 2004], but field data do not always support this [Johnson, 2004]. We  
83 do not investigate particle phase data in this work because it does not directly influence gas  
84 exchange rates across the air-sea interface and should be studied in its own right.

85 Figure 1 summarizes previously published observations of sea-air ammonia exchange. Note that  
86 throughout this paper, we use the convention of a positive flux being from sea to air (i.e. oceanic  
87 emission). Figure 1 only includes fluxes calculated from simultaneous measurements of  $\text{NH}_x$   
88 species in the atmosphere and ocean. Fluxes estimated from non-simultaneous measurements and  
89 early estimates using only an atmospheric *or* seawater concentration term [e.g. Georgii and  
90 Gravenhorst, 1977; Ayers and Gras, 1980] often give fluxes orders of magnitude greater than those  
91 observed in studies presenting simultaneous measurement, and are therefore discounted. We suggest  
92 the reasons for the differences between simultaneous and non-simultaneous observations are a) the  
93 high variability and rapid changes in concentrations of  $\text{NH}_x$  in all phases in space and time and b)  
94 the low quality and high detection limit of some of the early methods for measurements of  $\text{NH}_x$ ,  
95 particularly in the atmosphere [Johnson, 2004].

96 With the exception of the data of Asman *et al*, [1994], which were collected in the eutrophic and  
97 highly terrestrially- and anthropogenically-influenced North Sea, all previous studies suggest that  
98 sea-air ammonia exchange in the remote marine and pristine coastal environments is predominantly  
99 from sea to air. In this paper we present the first open-ocean dataset showing predominantly  
100 downward (into ocean) fluxes, from fieldwork at  $>55^\circ\text{N}$ . The reasons for such downward fluxes are  
101 identified and are compared to our data from two recent AMT (Atlantic Meridional Transect)  
102 cruises.

## 103 2. Fieldwork and methods

104 Data presented here originate from 6 research cruises, summarized in Table 1 and Figure 2. These  
105 cruises were ships of opportunity for the study of air-sea ammonia flux and as such, cruise track and  
106 sampling opportunities were not necessarily optimal for the work undertaken. Methods used and  
107 participating personnel during each cruise are listed in Table 2.

## 108 2.1 Seawater measurements

109

### 110 2.1.1 $\text{NH}_{\text{x}(\text{sw})}$

111 Total seawater ammonium concentration [ $\text{NH}_{\text{x}(\text{sw})}$ ] was measured by flow injection - gas diffusion -  
112 ion chromatography (FIGD-IC) *Gibb* [1994] during cruise PS211, an automated fluorescence  
113 method described by *Jones* [1991] during cruise AMT17; and the manual fluorescence method of  
114 *Holmes et al.*, [1999], during the remaining cruises.

115

116 Sampling was conducted from Niskin bottles attached to the CTD (Conductivity Temperature Depth  
117 profiler) frame (all cruises) and from the ships' non-toxic supply (NTS), intake at approximately 5m  
118 depth (S1801, JR75, D267 and AMT14). In general, excellent agreement was found between  
119 samples taken from Niskin bottles fired at the surface (0-3m depth) and simultaneously collected  
120 NTS samples from cruises S18/01, JR75 and D267 (Figure 3). These data suggest that sampling  
121 from the NTS is representative of the conditions in bulk surface seawater, at least during these  
122 cruises.

123

124

#### 125 FIGD-IC

126 All samples were analyzed unfiltered, within six hours of collection using flow injection gas  
127 diffusion-ion chromatography (FIGD-IC) as described in *Gibb et al.*, [1999]. In summary, sample  
128 was pumped continuously and treated with mixed EDTA (1.0 M) / NaOH (0.11 M) reagent to  
129 chelate alkaline earth cations and concurrently raise the pH of the mixture to >12. Under these  
130 conditions effectively all of the ammonium is deprotonated and able to diffuse from the sample  
131 stream, across a Goretex® membrane, into an acidic acceptor stream (40 mM MSA + sec-BA) in  
132 which they are re-protonated. Samples were concentrated by recirculation of the acceptor stream  
133 (20 mins) and then transferred to a Dionex DX-100 ion chromatograph (IC) and 200  $\mu\text{L}$  injected.  
134 This system can also be used for measurements of mono-, di- and tri-methylamines [e.g. *Gibb et al.*,  
135 1999]. The detection limit ( $2\sigma_{\text{n}}$  blank) was 28nM for ammonium. Response was linear ( $R^2 > 0.99$ , 0-  
136 1000 nM) and reproducibility (relative standard deviation, RSD) was 15.2% based on 20 nM  
137 standard addition to deep oceanic seawater.

138

#### 139 OPA (ortho-phthalaldehyde) methods

140

141 OPA fluorimetry is a recent method for the measurement of ammonium in natural waters, first  
142 presented for this use by *Jones* [1991] in an automated form, which has since been developed as a  
143 simple and effective manual method by *Holmes et al.*, [1999]. The principle reagent is ortho-  
144 phthalaldehyde (OPA – Sigma P-1378), which forms a fluorescent adduct on reaction with  
145 ammonium and primary amines. For ammonium assay, reaction with primary amines is inhibited by  
146 addition of sodium sulphite.

147

#### 148 Manual OPA method

149 The method of *Holmes et al.*, [1999] was followed closely and full details of the method can be  
150 found elsewhere [*Johnson et al.*, 2007]. In brief, OPA was introduced to samples in the form of a  
151 'working reagent', containing OPA in ethanol, di-sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7$ ) buffer and sodium  
152 sulphite, as described by *Holmes et al.*, [1999]. Water samples of approximately 25 ml were taken in  
153 clean 50 ml Corning centrifuge tubes and immediately inoculated with 2 ml working reagent. This  
154 working reagent to sample volume ratio was found to give a linear response to ammonium up to  
155 approximately 5  $\mu\text{M}$  (the highest observed concentration during these cruises study being  
156 approximately 2  $\mu\text{M}$ ). The fluorescence of the samples at 420 nm (after excitation at 380 nm) was  
157 measured using a Turner Designs 10AU fluorometer (AMT14) and a Jasco-750 spectrofluorometer  
158 (S18/01, JR75, D267), after the samples had been stored in the dark for a period of 3 to 24 hours .

159 During cruises S18/01 and JR75 measurement of sample concentration had standard uncertainty of  
160  $\pm 4.8\%$  (at  $\sim 95\%$  confidence) of sample concentration and a detection limit of approximately 2 nM.  
161 Reproducibility of replicates was less good during cruise D267 due to minor instrument  
162 malfunction, with a standard uncertainty of  $\pm 12.6\%$  and an effective detection limit of  $\sim 15$  nM.  
163 Full details of uncertainty analysis for these three cruises can be found in *Johnson* [2004]. Detailed  
164 quality control data is not available for the seawater  $\text{NH}_x$  measurements made during AMT14.  
165 However, sampling and analysis protocols used during AMT14 were identical to those on the  
166 previous cruises, so it is reasonable to assume that detection limit and precision are comparable.

## 167 **Automated OPA method**

168 During cruise AMT17 the automated method described by *Jones* [1991] was followed throughout.  
169 The detection limit for this technique was  $\sim 2$  nM and the precision was 8%.

## 170 **pH measurements**

171 Measurement of pH (seawater scale) was made during S18/01, JR75 and D267 following guidelines  
172 for calibrating and maintaining pH electrodes and sampling protocol for use at sea [*HELCOM*,  
173 2000]. Analysis of repeat measurements yields a precision of  $\pm 0.03$  pH units over the range of  
174 seawater pH.

175 Seawater scale pH was calculated from dissolved inorganic carbon (DIC) and total alkalinity (TA)  
176 data collected during AMT14, using the  $\text{CO}_2$  System Parameters Microsoft Excel macro developed  
177 by Dr. Denis Pierrot of NOAA AOML. This is a translation of the original CO2Sys.BAS program  
178 written by *Lewis and Wallace* [1998]. DIC and TA were determined using a VINDTA system  
179 (Marianda Co., Kiel, Germany). The DIC part of the system consists of a DIC extractor coupled to a  
180 coulometer (model 5011; UIC Coulometrics) which works in a similar fashion to the SOMMA  
181 system [*e.g. Johnson et al*, 1993]. The coulometer was calibrated twice daily using Certified  
182 Reference Materials (CRMs) supplied by Prof. Andrew Dickson (Scripps Institution of  
183 Oceanography). TA was determined by potentiometric titration in a thermostated open cell with  
184  $\sim 0.1\text{M}$  HCl in a  $0.7\text{M}$  NaCl solution. The Gran plot [*Gran*, 1952] and the constants of *Mojica*  
185 *Prieto and Millero* [2002] were used to calculate TA from the titration data. The strength of the acid  
186 was determined twice daily by titration against CRMs. Samples were collected and analyzed  
187 according to *DOE* [1994].

188 Where pH was not measured, (on cruises PS211 and AMT17, and occasional samples during the  
189 remaining cruises) a possible pH range (7.8-8.1) based on the data collected during cruises S1801,  
190 JR75 and AMT14, is assumed in calculating maximum and minimum possible air-sea fluxes from  
191 measured data (see below). This was not found to significantly affect the magnitude of the  
192 uncertainty in flux calculations relative to other uncertainties (gas phase measurement, integration  
193 over long periods, etc); i.e. within the constraints of commonly observed surface ocean pH values,  
194 quantifying pH accurately is not a major consideration compared to other uncertainties.

## 195 **2.2 Gas phase measurements**

196 Ammonia gas samples were collected on all five cruises using a filter pack technique. This  
197 technique, and the uncertainties associated with it are well documented and a review can be found  
198 elsewhere [*Johnson*, 2004]. Specific details of methods used on the different cruises considered  
199 here can be found in *Gibb et al*, [1999] (PS211), *Johnson* [2004] (S18/01, JR75 and D267), *Bell*  
200 [2006] (AMT14) and *Lesworth* [2007] (AMT17). In brief, the following is common to all cruises.

201 Aerosol and gas phase atmospheric samples were collected in tandem using a cyclonic filter-pack  
202 air-sampling technique [*Quinn et al*, 1988, 1990]. In summary, aerosols were collected on PTFE

203 pre-filters (47 mm diam., 1  $\mu\text{m}$  poresize; Costar, U.K.), whilst gaseous species were collected  
204 down-stream on pairs of oxalic acid-impregnated paper filters (47 mm diam., Whatman 40,  
205 Whatman Scientific, U.K.). Only gas phase measurements are considered in this paper.

206 Samples were collected in duplicate or triplicate filter-packs at flow rates of  $\sim 50 \text{ dm}^3 \text{ min}^{-1}$ , over  
207 periods of 10-100 hours from the monkey island (roof of the bridge) or equivalent forward-facing  
208 upper deck of the ship. Sampling was suspended during rain events, when the ship was not head-to-  
209 wind or when wind speed dropped below 5 knots. The volume of air sampled was determined by in-  
210 line gas meters (B.S.S., U.K.) situated between filter-pack and pump. In addition 'background'  
211 filter-packs were deployed, also consisting of one Teflon and two acidified paper filters, prepared  
212 and deployed as the sample filters but subject to zero air flow.  $\text{NH}_x$  was extracted from sample and  
213 blank filters into milli-Q ultrapure water and analysed using FIGD-IC (PS211) or the manual OPA  
214 method (S18/01, JR75, D267, AMT14, AMT17).

215 The dominant uncertainty in the filter pack technique used here was the large and variable blank  
216 value, and associated poor reproducibility in repeat measurements. The source of the blank  
217 variability is thought to have been contamination in the paper filters, possibly between acid-  
218 impregnation and deployment. Uncertainty due to blank variability was assessed on a per-sample  
219 basis for cruises PS211, S18/01, JR75 and D267 and ranged from  $\pm 0.75$  to  $\pm 3 \text{ nmol m}^{-3}$ .  
220 Uncertainty in measurements during AMT14 was quantified for all samples as  $\pm 2 \text{ nmol m}^{-3}$ .  
221 Substantial improvements in the system, particularly with respect to volume measurement, detailed  
222 in *Lesworth* [2007], led to a much smaller uncertainty of  $\pm 0.07 \text{ nmol m}^{-3}$  during AMT17.

223 A further problem with filter pack measurements specific to air-sea flux studies is the long  
224 integration time of the measurements. Over the sampling period of hours to days (and tens to  
225 hundreds of kilometers) seawater ammonium concentration is often highly variable, especially in  
226 summer when nitrogen is rapidly turned over by the mixed plankton community [*Johnson et al,*  
227 2007]. Thus, substantial uncertainty is introduced in the process of translation of a small number (1  
228 to 6) of discrete surface seawater measurements to an 'average' value appropriate for use with the  
229 integrated gas phase measurement. We have not found a completely rigorous method of assessing  
230 this uncertainty, particularly in the case of flux calculations using only one or two seawater  
231 measurements, which occurred predominantly on the cruises where seawater measurements were  
232 not conducted with air-sea flux calculations in mind (AMT 17), or where instrument problems  
233 meant limited seawater measurements (AMT 14). Instead, in calculating maximum and minimum  
234 possible fluxes we apply maximum and minimum observed values over an extended period around  
235 the atmospheric sampling period in question. This approach leads to large uncertainty ranges in  
236 some of the calculated fluxes; particularly those at lower latitudes where the flux is much more  
237 sensitive to seawater concentrations due to higher temperatures (see section 4). Nonetheless, in  
238 most cases (with the exception of AMT14 data, discussed in section 5), integrated fluxes are  
239 resolved at least to direction (i.e. into or out of the ocean), albeit often with a large range of possible  
240 magnitudes. This, however, is sufficient for the main purposes of this study.

## 241 2.3 Flux Calculation

242 Ocean-atmosphere fluxes of ammonia are calculated as a function of the deviation from predicted  
243 Henry's Law equilibrium between measurements of  $(\text{NH}_3(\text{g}))$  in the marine boundary layer and  
244 values of  $[\text{NH}_3(\text{sw})]$ , calculated from measured  $[\text{NH}_x(\text{sw})]$  in surface seawater. Ammonia is a soluble  
245 gas and its transfer is generally considered to be under gas phase control [*Liss, 1983*]. There is some  
246 evidence that under conditions of extreme surface water stability (such as those observed in  
247 stagnant, short fetch waters) there is a water-phase component to the rate of transfer across the air-  
248 water interface [*e.g. Trevvit et al, 1988*]. However, this is not thought to be applicable to the open  
249 ocean situation. The flux of ammonia across the ocean-atmosphere interface can be calculated

250 according to (1) [Liss and Slater, 1974].

$$251 \quad F = k_g \cdot \{(\text{NH}_3(\text{g})) - K_H \cdot [\text{NH}_3(\text{sw})]\} \quad (1)$$

252 where  $F$  is the ocean-atmosphere flux ( $\text{pmol m}^{-2} \text{s}^{-1}$ ),  $k_g$  is the gas phase transfer velocity ( $\text{m s}^{-1}$ ) and  
253  $K_H$  is the dimensionless Henry's Law coefficient for ammonia (i.e. the ratio of *gas phase* to *liquid*  
254 *phase* concentration at equilibrium). The concentrations of gas phase and dissolved ammonia must  
255 be in the same units (in this case  $\text{pmol m}^{-3}$ ).

256 The gas phase transfer velocity is calculated as a function of wind speed according to [Duce et al,  
257 1991] (2).

$$258 \quad k_g = u / [770 + 45 \times (\text{RMM})^{1/3}] \quad (2)$$

259 where  $u$  is the wind speed ( $\text{m s}^{-1}$ ) and RMM is the relative molecular mass of the gas (17.03 in the  
260 case of ammonia). The concentration of dissolved non-solvated ammonia is given by (3):

$$261 \quad [\text{NH}_3(\text{sw})] = [\text{NH}_x(\text{sw})] \cdot K_a / (K_a + [\text{H}^+]) \quad (3)$$

262 Where  $[\text{NH}_x(\text{sw})]$  is in the units of  $\text{pmol m}^{-3}$ ,  $[\text{H}^+] = 10^{-\text{pH}}$  and  $K_a = 10^{-\text{pK}_a}$ .  $\text{pK}_a$  is calculated according  
263 to Johansson and Wedborg [1980], from measured values of the dissociation of ammonium in  
264 seawater (4):

$$265 \quad \text{pK}_a = -0.467 + (0.00113 \cdot S) + (2887.9 / T) \quad (4)$$

266 Where  $S$  is the salinity (unitless) and  $T$  is the temperature in  $^\circ\text{C}$ . The Henry's law coefficient,  $K_H$ , is  
267 calculated according to [McKee, 2001; Johnson et al, 2007](5).

$$268 \quad K_H = [17.93 \times (T/273.15) \times e^{(4092/T) - 9.70}]^{-1} \quad (5)$$

269 Presented in the literature are many apparently different methods to calculate air-sea ammonia  
270 exchange using the concentration difference approach (i.e. equation 1) [e.g. Quinn et al, 1988,  
271 1990, 1992; Asman et al, 1994; Gibb et al, 1999], using different formulations for calculating  $K_H$   
272 and  $k_g$ . However, all the methods where the  $T$  and  $S$  dependence of  $K_H$  and  $K_a$  are accounted for are  
273 numerically very similar (agreeing to within  $\pm 2\%$  under most conditions [Johnson, 2004]), so we  
274 consider fluxes calculated using the above equations directly comparable to the studies listed above  
275 and presented in Figure 1. Note that in some earlier flux calculations [e.g. Georgii and Gravenhorst,  
276 1977] the effect of temperature is not accounted for, which is a major failing in light of the findings  
277 we present in Section 4.

278 A number of studies of air-sea ammonia flux have used a formula for  $\text{pK}_a$  in seawater presented in  
279 Khoo et al, [1977]. Whilst the tabulated data presented in their manuscript are in very close  
280 agreement with other studies of ammonium dissociation e.g. Johansson and Wedborg [1980], the  
281 formula they quote as representing their measured data is in fact substantially divergent from it, and  
282 fundamentally flawed [Bell et al, 2007]. Whilst this has a substantial effect on the sensitivity of the  
283 air-sea ammonia flux to temperature at a given seawater ammonium concentration (see Section 4),  
284 it is probably not of great significance in previous air-sea ammonia flux studies in comparison with  
285 the uncertainties introduced by filter pack measurements of gas phase ammonia, or uncertainty due  
286 to variable seawater  $\text{NH}_x$  concentration during atmospheric sampling.

### 287 **3 Results from high latitude cruises**

288

289 Surface seawater and atmospheric data collected during the four high latitude cruises are  
290 summarized in Table 3, along with air and seawater concentration data reported in previous studies  
291 in similar regions for comparison.

292 Note that there is no apparent seasonal trend in the gas phase ammonia data presented in Table 3. If  
293 there is such a trend in marine background concentrations, it is most likely being masked in this  
294 dataset by the advection of NH<sub>x</sub>-rich air from Europe and America; and possibly from volcanic  
295 sources near Iceland during cruise D267 [Johnson, 2004]. However, lower concentrations were  
296 measured during these cruises than have previously been observed in the region (Table 3). In fact,  
297 the gas phase data presented here suggests that concentration ranges observed in this region are well  
298 constrained compared to nearby terrestrial environments, where concentrations can vary over many  
299 orders of magnitude. The minimum concentration of gas phase ammonia observed during each of  
300 the first three cruises was 1.4 nmol m<sup>-3</sup>. This agreement is coincidental and does not represent the  
301 limit of detection or other methodological limit of filter pack sampling during these cruises.

302 Higher concentrations of ammonium appear to occur in seawater in summer and autumn than in  
303 winter cruises. This is corroborated in a larger dataset of observed seawater ammonium  
304 concentrations in the region presented in Johnson [2004], that finds low (<100 nM) concentrations  
305 occur most frequently and with similar regularity during cruises in all seasons, with concentrations  
306 reaching substantially greater peak values in the summer when the recycling of nitrogen is at its  
307 most rapid. As we suggest in Johnson *et al.*, [2007], these peaks are likely associated with the  
308 temporary decoupling of uptake and remineralisation processes during e.g. a crash in the  
309 autotrophic community due to non-nitrogenous nutrient limitation. During periods of nitrogen  
310 limitation, however, concentrations are likely to be consistently low (< 100nM) as the community  
311 will efficiently re-use NH<sub>x</sub> as a 'cheap' source of reduced N. This is more in keeping with  
312 concentrations commonly observed in oligotrophic gyre regions (Section 5), and may be the  
313 nitrogen 'regime' observed by Rees *et al.*, [2001] and Rees *et al.*, [2002], where consistently low  
314 concentrations were observed in the northern North Sea and NE Atlantic.

315  
316 Note that the dataset from cruise PS211 is uncharacteristically devoid of <50 nM concentrations of  
317 surface NH<sub>x</sub>, which may be due to the accumulation of ammonium in surface waters associated with  
318 the decline of the summer phytoplankton community. Chlorophyll-*a* levels (not shown) were  
319 relatively high during PS211, particularly in more northerly waters (up to 1 mg l<sup>-1</sup>) where  
320 ammonium was depleted relative to more southerly waters, possibly due to the onset of the autumn  
321 bloom associated with mixing of nutrients from below the seasonal thermocline. There are no other  
322 open-ocean data from the North Atlantic or other comparable waters during this phase of the  
323 seasonal cycle. However, it is possible the data from PS211 are representative of persistently  
324 elevated surface NH<sub>x</sub> occurring during the late summer / autumn as heterotrophs dominate the  
325 microbial community and photosynthesisers decline.

326 Figure 4 presents data collected during the 4 high latitude cruises (PS211, S1801, JR75 and D267).  
327 Sea-air fluxes are plotted as boxes, such that their vertical spread represents a range of possible  
328 values based on the measured data; the greatest uncertainties being those associated with (a) filter  
329 pack gas phase measurements (section 2.2) and (b) the uncertainty in translating a small number of  
330 discrete seawater measurements into an 'average' value for the duration of the gas phase sampling  
331 (section 2.3). The box widths represent the latitudinal range over which the gas phase samples (and  
332 thus fluxes) were integrated. Note that this varies from <0.1 degrees of latitude (samples taken  
333 when the ship was on station and head-to-wind for an extended period), to >3 degrees in situations  
334 where the ship was steaming between stations and gas phase samples were collected over relatively  
335 long (>24 hour) periods.

336  
337 Whilst there is large variability in the magnitude and direction of the fluxes associated with gas

338 phase and water phase concentrations, it is clear from Figure 4 that all of the calculated fluxes at  
339  $>55^\circ\text{N}$  are likely to be from air-to-sea (i.e. negative). The few flux ranges whose upper extent  
340 crosses into positive (sea-to-air) sit mostly in the negative. In all but 2 cases the possible positive  
341 values are associated with gas phase measurements for which the uncertainty in measurement is  
342 greater than the absolute concentration i.e. effectively below detection limit, and thus the lower  
343 value of gas phase concentration used in the flux calculation is zero (in which case a positive flux is  
344 inevitable). As we will demonstrate in Section 4, a relatively small gas phase concentration ( $<1$   
345  $\text{nmol m}^{-3}$ ) is required to balance an 'average' ambient seawater  $\text{NH}_x$  concentration of  $100\text{nM}$  at  
346  $10^\circ\text{C}$  (the typical temperature observed during cruises S1801 and JR75, where possible upward  
347 fluxes are predicted). Thus it is unlikely that these flux ranges represent real upward fluxes. The  
348 remaining 2 data that predict possible upward fluxes (in the Greenland Sea during cruise JR75) are  
349 associated with the two highest surface  $\text{NH}_x$  concentrations ( $\sim 600 - 650\text{ nM}$ ) observed over all 6  
350 cruises presented in this paper. These exceptionally high surface values were observed during the  
351 spring bloom and, as we demonstrate in *Johnson et al.*, [2007], such high concentrations are likely to  
352 be transient phenomena associated with temporary decoupling of uptake and regeneration processes  
353 during bloom conditions. As such they may lead to sporadic emission of ammonia from surface  
354 seawater, but are not likely to be representative of year-round conditions. Thus we conclude from  
355 the above data that at above  $\sim 55^\circ\text{N}$  the direction of ammonia flux across the air-sea interface is  
356 almost exclusively from air to sea in the high latitude North Atlantic and that these regions are  
357 likely to be a net sink for atmospheric  $\text{NH}_3$  on an annual timescale, in spite of possible occasional  
358 emission events associated with e.g. phytoplankton bloom decline [*Johnson et al.*, 2007]. It is worth  
359 noting here that shallow shelf seas (e.g. the southern bight of the North Sea) typically have  
360 substantially greater surface  $\text{NH}_x$  concentrations [*Johnson*, 2004] and may therefore be a source of  
361 ammonia to the atmosphere at latitudes where the open ocean is likely to be a sink. However, this is  
362 not clear cut - such areas are close to the coast and thus the overlying air may be strongly influenced  
363 by terrestrial ammonia sources. For example, observations in the southern North Sea by *Asman et al.*  
364 [1994] suggest that the magnitude and direction of the flux varies with local surface seawater  
365 and gas phase concentrations, which are dependent on e.g. source region and amount of recent  
366 precipitation (rain events tending to strip gas and particle phase  $\text{NH}_x$  from the atmosphere).

#### 367 4 Sensitivity analysis

368 In this section we present evidence that the reason for the observed downward fluxes in the high  
369 latitude North Atlantic is the temperature dependence of the equilibrium between  $\text{NH}_x$  in surface  
370 seawater and gas phase  $\text{NH}_3$  in the overlying atmosphere. Figure 5 demonstrates the sensitivity of  
371 this equilibrium to salinity, pH and temperature, over ranges commonly observed in the surface  
372 ocean. It is clear that the sensitivity to temperature considerably outweighs the others, and that  
373 salinity is the least important of the three factors in determining the direction and magnitude of air-  
374 sea flux. For example, a normal seawater  $\text{NH}_x$  concentration of  $100\text{ nM}$  will be 'balanced' (i.e. to  
375 give a zero net flux) by a gas phase concentration of  $0.77\text{ nmol m}^{-3}$  at  $10^\circ\text{C}$ , so given a gas phase  
376 'background' concentration of  $1-3\text{ nmol m}^{-3}$  (Table 3), the resulting flux will be negative (i.e. from  
377 air to sea). Conversely, at temperature  $T=30^\circ\text{C}$ , the same seawater concentration requires a gas  
378 phase concentration of  $8.31\text{ nmol m}^{-3}$  to balance the flux, and thus at typical ambient concentration  
379 the flux will be out of the ocean.

380 Note that according to Equation 5, the Henry's law coefficient does not show variation with salinity.  
381 However, included in the formulation (presented by *McKee* [2001], after *Gibb et al.*, [1999]) is a  
382 correction to account for the "20% decrease in solubility of gases in seawater" compared to  
383 freshwater (after *Stumm and Morgan* [1981]). We thus calculate the zero salinity line in Figure 5(c)  
384 by removing this correction (as well as calculating changes to  $\text{pK}_a$ ). This demonstrates that, whilst  
385 this 20% solubility correction is a rather simplistic assumption, for the purposes of this and similar  
386 studies it can be considered a minor uncertainty in calculating fluxes.

387  
388 The temperature sensitivity shown in Figure 5(a) is a function of the T dependence of both the  
389 solubility of NH<sub>3</sub> (i.e. K<sub>H</sub>) and the acid dissociation of NH<sub>4</sub><sup>+</sup> (i.e. pK<sub>a</sub>). It is useful to identify the  
390 relative contributions of each of these terms to the overall temperature sensitivity. The gas phase  
391 equilibrium concentration represented by the term K<sub>H</sub>·[NH<sub>3(sw)</sub>] in Equation (1) and denoted  
392 (NH<sub>3(g)eq</sub>), i.e. the gas phase concentration that would be in equilibrium with a given seawater  
393 concentration, can be expressed according to (6) as:

$$394 \quad (\text{NH}_{3(\text{g})\text{eq}}) = K_{\text{H}} \cdot [\text{NH}_x] \cdot K_{\text{a}}^* \quad (6)$$

395 where K<sub>a</sub><sup>\*</sup> is a unitless representation of the speciation of the ammonium-ammonia equilibrium (7):

$$396 \quad K_{\text{a}}^* = K_{\text{a}}/(\text{K}_{\text{a}} + [\text{H}^+]) \quad (7)$$

397 Both K<sub>H</sub> and K<sub>a</sub><sup>\*</sup> show an increase with temperature over the range 0 – 35 °C; with K<sub>H</sub> increasing  
398 from 2.8x10<sup>-4</sup> to 1.4x10<sup>-3</sup> (an approximate 5-fold increase) and K<sub>a</sub><sup>\*</sup> increasing from 0.007 to 0.102  
399 (an approximate 15-fold increase). Thus, over the range of temperatures considered here, change in  
400 the ammonium-ammonia equilibrium is ~3 times more important to the temperature dependence of  
401 sea-air ammonia flux than the Henry's Law constant. However it is the product of both effects  
402 together (a factor of 75) that makes the T dependence so strong overall. It is worth noting that at  
403 lower temperatures (up to 20 °C) the contributions of the two components to temperature sensitivity  
404 are similar. It is at higher temperatures, i.e. at lower latitudes, where K<sub>a</sub><sup>\*</sup> dominates.

## 405 **5 Results from Atlantic Meridional Transect (AMT) cruises**

406 We have identified that temperature is a fundamental control on the magnitude and direction of sea-  
407 air ammonia flux. Further, it seems that the temperature dependence alone can explain the  
408 differences between the high latitude observations presented above (where almost all fluxes were  
409 negative, i.e. from air to sea) and all previous open-ocean studies (conducted at latitudes of <50°  
410 and showing fluxes almost exclusively from sea to air). Table 4 presents the seawater and gas phase  
411 concentration data collected during the AMT cruises, along with data from other studies in similar  
412 regions and at similar latitudes for comparison.

413 The seawater and atmospheric concentrations measured during cruises AMT14 and AMT17 are  
414 within the range of previously observed concentrations, which are reasonably consistent between  
415 studies. In general the observed concentrations (especially mean and minimum concentrations) are  
416 lower than those observed at high latitudes (Table 3). This is presumably due to the generally  
417 nutrient-limited surface waters at low latitudes, where stratification limits nutrient supply from  
418 depth. We do not include seasonal information in Table 4 as there is no apparent pattern in  
419 ammonium concentration, i.e. with the limited available data, regional or transient variability  
420 outweighs seasonal variability.

421 In the atmosphere there is similarly no obvious trend with seasons. The high resolution data of  
422 *Norman and Leck* [2005] demonstrates apparent high regional variability. However, as they  
423 highlight in their paper, air mass source region is of key importance with, for example, high  
424 concentrations strongly associated with biomass burning in their case.

425 The data presented by *Quinn et al.*, [1990] from the central Pacific, show strong fluxes of ammonia  
426 out of the ocean. This could be explained, without the need to invoke the temperature sensitivity  
427 outlined above, by the extremely low gas phase concentrations during their study (commonly below  
428 the detection limit of 0.01 nmol m<sup>-3</sup>). However, we present data in this section with substantially  
429 greater gas phase concentrations that also demonstrate predominantly upward fluxes.

430 Data from the two AMT cruises is presented in Figure 6. Data from AMT17 demonstrate that sea to  
431 air fluxes dominate at low latitudes, in spite of much lower average seawater concentrations than  
432 those observed during the high latitude cruises (Figure 4). The uncertainty in the magnitude and  
433 direction of calculated fluxes is more than one order of magnitude larger for AMT14 than AMT17.  
434 This is partly due to the much higher quality gas phase measurements during AMT17 as a result of  
435 the method improvements outlined in Section 2.2. However, the uncertainty in the calculated fluxes  
436 is also substantially greater in the AMT14 data due to the relatively high variability of the seawater  
437 concentrations: during AMT17, surface seawater  $\text{NH}_x$  concentrations rarely exceeded 30 nM, with  
438 the majority of measurements below 10 nM. In contrast, during AMT14 the concentrations changed  
439 rapidly throughout the cruise, commonly varying between  $<5$  nM and  $>150$  nM over the course of a  
440 single atmospheric sample. In this case it is extremely difficult to constrain the 'average' seawater  
441 concentration over the course of the atmospheric sampling time and uncertainties are consequently  
442 very large. As with most other cruise data sets, e.g. as assessed in *Johnson* [2004], including all of  
443 the cruises presented here, no relationships between surface ammonium concentration and other  
444 routinely measured state variables (such as chlorophyll, nutrient concentrations, temperature or  
445 salinity) could be found to constrain the uncertainty associated with the integration of seawater  
446 measurements over the atmospheric sampling period.

447 It is noticeable that the flux data from AMT14 is 'skewed': the mean calculated fluxes sit well  
448 below the central point of each possible flux range in the data from less than 40 degrees of latitude  
449 in both hemispheres. This is due to the highly variable seawater concentrations; specifically that the  
450 mean seawater concentrations happen to be biased towards the lower values. Due to the sparseness  
451 of data relative to their high variability, mean flux values for AMT14 should be considered highly  
452 uncertain.

453 The maximum predicted upward fluxes from the AMT14 dataset are more than an order of  
454 magnitude greater than those predicted from AMT17. However, they are of the same order as the  
455 maximum fluxes observed in the central Pacific by *Quinn et al*, [1990] (Figure 1) and thus not  
456 unreasonable. The fluxes predicted from AMT17 data are extremely low in comparison to other  
457 studies (few fluxes of greater than  $\pm 10$  pmol  $\text{m}^{-3}$  between 40 °N and 40 °S), demonstrating that  
458 under the observed conditions, ocean and atmosphere were relatively close to equilibrium with  
459 respect to ammonia.

460 The extremely low and consistent seawater concentrations observed during AMT17 highlight the  
461 importance of temperature for air-sea ammonia flux, when compared with the data of *Quinn et al*,  
462 [1990]. Both observe similar gas phase ammonia concentrations (average in both cases  $<1$  nmol  $\text{m}^{-3}$ ,  
463 with minimum observed concentrations one order of magnitude lower) at similar latitudes in the  
464 Atlantic and Pacific. However, the seawater concentrations on AMT17 rarely exceeded 20 nM in  
465 the gyre and equatorial regions, whereas the *Quinn et al*, [1990] seawater concentrations were in the  
466 range 100 to 700 nM; one order of magnitude greater. In spite of the much lower seawater  
467 concentrations during AMT17, fluxes out of the ocean are still observed, which must be due to the  
468 strong temperature dependence of ammonia solubility and base dissociation. However, it is worth  
469 noting that when gas phase concentrations during AMT17 were higher than the apparent  
470 background of  $<0.1$  nmol  $\text{m}^{-3}$ , fluxes occasionally stray into the negative (i.e. an ocean sink). So,  
471 whilst the temperature dependence appears to be very important in the global trends in air-sea  
472 ammonia flux, it can be dominated by local or regional biogeochemical effects (e.g. biological  
473 controls on seawater concentrations, long range transport of  $\text{NH}_3$ , etc), particularly at low  
474 concentrations when the system is close to equilibrium.

475 An important difference to note between AMT14 and AMT17 data (Figure 6) is the direction of the  
476 fluxes at  $>40$  °N, where predicted fluxes during AMT14 are almost exclusively negative, and during  
477 AMT17 almost exclusively positive. This region was covered in spring by AMT14 and autumn by

478 AMT 17. Thus this difference is consistent with our suggestion above that autumn is likely to be a  
479 key time for ammonia emission events at higher latitudes, when summer communities die back and  
480 ammonium accumulates, and when waters are at their annual maximum temperature.

481 Interestingly, higher seawater concentrations during AMT14 are complemented by higher gas phase  
482 concentrations, leading to apparent closeness to equilibrium within the large uncertainties in  
483 calculated fluxes (i.e. many predicted minimum fluxes stray into the negative). The reason for the  
484 higher concentrations in both phases is unknown; however we speculate that in seawater, elevated  
485 concentrations may relate to the cruise tracks of AMT14 and AMT17. AMT 17 went further into the  
486 N. Atlantic subtropical gyre (further from terrestrial influence and further into nutrient limitation),  
487 and, in heading east to S. Africa went through the S. Atlantic subtropical gyre, avoiding the  
488 productive Falklands shelf area encountered in AMT14.

489 The enhanced gas phase concentrations observed during AMT14 can be explained by the influence  
490 of terrestrial sources of ammonia. During AMT14, back trajectory analysis and chemical  
491 characterization reveals the influence of biomass burning in many of the atmospheric samples [Bell,  
492 2006]. Biomass burning is identified by Norman and Leck [2005] as the source of the highest  
493 observed atmospheric ammonia concentrations (up to  $\sim 18 \text{ nmol m}^{-3}$ ). Similar analysis reveals that  
494 extremely clean air masses were sampled during AMT17 [Lesworth, 2007], with only 7 of  $\sim 30$   
495 atmospheric samples having passed over land in the 5 days previous to sampling, and none of these  
496 over strong biomass burning source regions. It is possible that terrestrial inputs (of nitrogen or other  
497 essential nutrients) to the ocean during AMT14 stimulated biological activity in the ocean leading to  
498 the elevated ammonium concentrations in seawater. However, the data necessary to test this  
499 hypothesis are unavailable.

## 500 **6 Conclusions**

501 We present strong evidence that the high latitude oceans are a sink for gas phase ammonia and  
502 identify that the reason for this is the temperature dependence of air-sea ammonia flux. Further, we  
503 demonstrate that remote oligotrophic regions away from terrestrial atmospheric influence are  
504 relatively close to equilibrium between ocean and atmosphere with respect to ammonia but that  
505 these regions are still probably a net source of ammonia to the atmosphere in spite of extremely low  
506 seawater concentrations. This is in contrast with the high latitude North Atlantic, where surface  
507 seawater concentrations are more than one order of magnitude greater, but fluxes are downwards  
508 due to lower temperatures.

509 A picture thus emerges of the global ocean being a source of ammonia at low latitudes and a sink at  
510 high latitudes, which is demonstrated in the summary of field data from this study in Figure 7. This  
511 is somewhat counter-intuitive, as high latitudes have greater primary productivity, greater reduction  
512 of nitrogen and as a consequence higher ammonium concentrations. A paper dedicated to the  
513 quantification of budgets of air-sea ammonia flux based on the observations presented here is  
514 currently in preparation.

515 In order to improve our understanding of the air-sea exchange of ammonia, an atmospheric method  
516 for measuring  $\text{NH}_3$ , such as that used by Norman and Leck [2005], which operates at a much higher  
517 resolution than filter packs (sample integration time of minutes rather than hours or days) is  
518 required, used in tandem with simultaneous measurements of surface seawater concentrations. This  
519 will enable 'point' measurements of fluxes and reveal finer detail such as diurnal cycles, as well as  
520 better constraining uncertainty in fluxes by bringing the timescale of atmospheric and surface  
521 seawater measurements closer together.

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533

533 **References**

- 534 Asman, W. A. H., R.M. Harrison et al, Estimation of the net air-sea flux of ammonia over the  
535 southern bight of the North Sea, *Atmospheric Environment*, 28, 3647-3654, 1994.
- 536 Ayers, G. P., and J. L. Gras, Ammonia gas concentrations over the Southern Ocean, *Nature*, 284,  
537 539-540, 1980.
- 538 Bell, T.G., *Dimethylsulphide and ammonia in remote marine regions – an Atlantic Meridional*  
539 *Transect study*, PhD Thesis, University of East Anglia, Norwich, UK, 2006.
- 540 Bell, T. G., M. T. Johnson, P. S. Liss and T. D. Jickells, Ammonia/ammonium dissociation  
541 coefficient in seawater: A significant numerical correction, *Environmental Chemistry*, 4, 183-186,  
542 2007.
- 543 Blackall, T. D., L.J. Wilson, M.R. Theobald et al, Ammonia emissions from seabird colonies,  
544 *Geophysical Research Letters*, 34, doi:10.1029/2006GL028928, 2007.
- 545 Brzezinski, M. A., Vertical distribution of ammonium in stratified oligotrophic waters, *Limnology*  
546 *and Oceanography*, 33, 1176-1182, 1988.
- 547 DOE, *Handbook of methods for the analysis of the various parameters of the carbon dioxide*  
548 *system in sea water*, edited by A. G. Dickson and C. Goyet, ORNL/CDIAC-74, 1994
- 549 Duce, R. A., P. S. Liss, et al, The atmospheric input of trace species to the world ocean, *Global*  
550 *Biogeochemical Cycles*, 5(3), 193-259, 1991.
- 551 Edmunds, H. M., *The seasonal cycle of dissolved inorganic nutrients in the southern North Sea*  
552 *during 1988/1989*, Mphil thesis, School of Environmental Sciences, University of East Anglia,  
553 Norwich, UK, 1991.
- 554 Geerneart, L. L. S., G. L. Geerneart et al, Fluxes of soluble gases in the marine atmosphere surface  
555 layer, *Tellus B*, 50, 111-127, 1998.
- 556 Georgii, H. W., and G. Gravenhorst, The oceans as a source of sink of reactive trace gases, *Pure and*  
557 *Applied Geophysics*, 115, 503-511, 1977.
- 558 Gibb, S. W., *Trace Determination of Ammonia and Methylamines by Flow Injection Extraction –*  
559 *Ion Chromatography in Estuarine and Marine Environments*, PhD Thesis, University of East  
560 Anglia, Norwich, UK, 1994.
- 561 Gibb, S. W., P. S. Liss and R. F. C. Mantoura, Ocean-atmosphere exchange and atmospheric  
562 speciation of ammonia and methylamines in the region of the NW Arabian Sea, *Global*  
563 *Biogeochemical Cycles*, 13, 161-178, 1999.
- 564 Glibert, P. M., M. R. Dennett et al, Nitrogen uptake and NH<sub>4</sub><sup>+</sup> regeneration by pelagic  
565 microplankton and marine snow from the North Atlantic, *Journal of Marine Research*, 46, 837-852,  
566 1988.
- 567 Gran, G., Determination of the equivalence point in potentiometric titrations, part II, *Analyst*, 77,  
568 661-671, 1952.
- 569 Harrison, W. G., E. J. H. Head et al, The Western North Atlantic Bloom Experiment, *Deep Sea*  
570 *Research Part II*, 40, 279-305, 1993.
- 571 HELCOM, Annex B-14 Technical notes on the measurement of pH in seawater, *Manual for Marine*  
572 *Monitoring in the COMBINE program of Helcom*, Helsinki, 2000.
- 573 Holmes, R., A. Aminot et al, A simple and precise method for measuring ammonium in marine and  
574 freshwater ecosystems, *Canadian Journal of Fisheries and Aquatic Science*, 56, 1801-1808, 1999.
- 575 Johansson, O. and M. Wedborg, Ammonia-ammonium equilibrium in seawater at temperatures  
576 between 5 and 25 °C, *Journal of Solution Chemistry*, 9, 37-44, 1980.

- 577 Johnson, K. M., K. D. Wills, D. B. Butler, W. K. Johnson and C. S. Wong, Coulometric total carbon  
578 dioxide analysis for marine studies: maximising the performance of an automated continuous gas  
579 extraction system and coulometric detector, *Marine Chemistry*, 44, 167-187, 1993.
- 580 Johnson, M. T., *The Air-sea Flux of Ammonia*, PhD Thesis, University of East Anglia, Norwich,  
581 UK, 2004.
- 582 Johnson, M.T., R. Sanders et al, Ammonium accumulation during a silicate limited diatom bloom  
583 indicates the potential for ammonia emission events, *Marine Chemistry*, 106, (1-2), 63-75, 2007.
- 584 Jones, R.D., An improved fluorescence method for the determination of nanomolar concentrations  
585 of ammonium in natural waters, *Limnology and Oceanography*, 36, 814-819, 1991.
- 586 Khoo, K. H., C. H. Culberson et al, Thermodynamics of the dissociation of ammonium ion in  
587 seawater from 5 to 40°C, *Journal of Solution Chemistry*, 6(4), 281-290, 1977.
- 588 Le Bouteiller, A., Environmental control of nitrate and ammonium uptake by phytoplankton in the  
589 equatorial Atlantic *Ocean*, *Marine Ecology Progress Series*, 30, 167-179, 1986.
- 590 Lebel, P. J., J.M. Hoell et al, Aircraft measurements of ammonia and nitric acid in the lower  
591 troposphere, *Geophysical Research Letters*, 12(6), 401-404, 1985.
- 592 Lesworth, T. *Atmospheric inputs to the North Atlantic*, PhD thesis, University of East Anglia,  
593 Norwich, UK, 2007.
- 594 Lewis, E., and D. W. R. Wallace, *Program developed for CO<sub>2</sub> system calculations*, ORNL/CDIAC-  
595 105, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S.  
596 Department of Energy, Oak Ridge, Tennessee, 1998.
- 597 Liss, P. S. and P. G. Slater, Flux of gases across the air-sea interface, *Nature*, 247, 181-184, 1974.
- 598 Liss, P. S., Gas transfer: Experiments and geochemical implications, in *Air-Sea Exchange of Gases  
599 and Particles*, edited by P. S. Liss, W. G. N. Slinn, D. Reidel, Dordrecht, p241-298, 1983.
- 600 Liss, P.S. and J.N. Galloway, Air-sea exchange of sulphur and nitrogen and their interaction in the  
601 marine atmosphere, in *Interactions of C, N, P and S Biogeochemical Cycles and Global Change*,  
602 edited by R. Wollast, F. T. Mackenzie and L. Chou. Springer-Verlag, Berlin, 259-281, 1993.
- 603 Longhurst, A. R., A. Bedo et al, Nflux – a test of vertical nitrogen flux by diel migrant biota, *Deep  
604 Sea Research A*, 36(11), 1705-1719, 1989.
- 605 McKee, C. M., *Biogeochemical Cycles of Ammonia and Dimethylsulphide in the Marine  
606 Environment*, PhD thesis, University of East Anglia, Norwich, UK, 2001.
- 607 Mojica Prieto, F. J. and F. J. Millero, The values of pK<sub>1</sub> and pK<sub>2</sub> for the dissociation of carbonic  
608 acid in seawater, *Geochemica et Cosmochemica Acta*, 66 (14), 2529-2540, 2002.
- 609 Norman, N and C. Leck, Distribution of marine boundary layer ammonia over the Atlantic and  
610 Indian Oceans during the Aerosols99 cruise, *Journal of Geophysical Research*, 110, D16302, 2005.
- 611 Ottley, C. J. and R. M. Harrison, The spatial distribution and particle size of some inorganic  
612 nitrogen, sulphur and chlorine species over the North Sea, *Atmospheric Environment*, 26A(9), 1689-  
613 1699, 1993.
- 614 Quinn, P. K., *Simultaneous Observations of Ammonia in the Ocean and Atmosphere in the Remote  
615 Marine Environment*, PhD thesis, University of Washington, USA, 1988.
- 616 Quinn, P. K., T.S. Bates et al, Interactions between the sulphur and reduced nitrogen cycles over the  
617 central Pacific Ocean, *Journal of Geophysical Research*, 95(D10), 16405-16416, 1990.
- 618 Quinn, P. K., A. E. Asher et al, Equilibria of the marine multiphase ammonia system, *Journal of  
619 Atmospheric Chemistry*, 14, 11-30, 1992.
- 620 Quinn, P. K., K. J. Barrett et al, Estimation of the air/sea exchange of ammonia for the North

- 621 Atlantic Basin, *Biogeochemistry*, 35, 275-304, 1996.
- 622 Rees, A. P., I. Joint et al, Carbon, nitrogen and phosphorous budgets within a mesoscale eddy:  
623 comparison of mass balance with in vitro determinations, *Deep Sea Research part II*, 48, 859-872,  
624 2001.
- 625 Rees, A. P., E. M. S. Woodward et al, Size-fractionated nitrogen uptake and carbon fixation during a  
626 developing coccolithophore bloom in the North Sea during June 1999, *Deep Sea Research part II*,  
627 49, 2905-2927, 2002.
- 628 Stumm, W. and J. J. Morgan, *Aquatic Chemistry*, Wiley Interscience, Ney York, 1981.
- 629 Theobald, M. R., P. D. Crittenden et al, Ammonia emissions from a Cape fur seal colony, Cape  
630 Cross, Namibia, *Geophysical Research Letters*, 33, doi:10.1029/2005GL024384, 2006.
- 631 Trevvit, A. C. F., Freney, J. R., Denmead, O. T. et al. Water-air transfer resistance for ammonia from  
632 flooded rice, *Journal of Atmospheric Chemistry*, 6, 133-147, 1988.
- 633 Ueamatsu, M., M. Torantini, M. Kajino, Y. Narita, Y. Senga, and T. Kimoto, Enrichment of primary  
634 production in the western North Pacific caused by the eruption of Miyake-jima volcano,  
635 *Geophysical Research Letters*, 31, L06106, doi:10.1029/2003GL018790, 2004.
- 636 Warneck, P, *Chemistry of the Natural Atmosphere*, Academic Press, 1988.
- 637

637 **Figure Captions**

Figure 1: Summary of data presented by previous studies of air-sea ammonia flux. Only data from simultaneous measurements of seawater and gas phase species is considered.

Figure 2. Tracks of the 6 cruises from which data is presented. Table 1 provides further details. Plot produced using the freely-available **Ocean Data View** (<http://odv.awi-bremerhaven.de/home.html>).

Figure 3: Comparison of simultaneous measurements of NTS (non-toxic supply) and CTD (Niskin)  $\text{NH}_x$  concentration from cruises S18/01, JR75 and D267. Error bars represent approximately 95% confidence limits in the measured data. No such comparable data were available for the remaining cruises.

638

639 Figure 4: Data from the high latitude cruises conducted during this study. **A:** Gas phase data;  
640 vertical extent of each box corresponds to uncertainty in measurement at an approximate 95%  
641 confidence interval. Horizontal extent represents the latitudinal range over which samples were  
642 collected. **B:** Surface seawater ammonium concentration. For simplicity, error bars are not presented  
643 on these data, as the uncertainty is negligible in air-sea flux calculation relative to the other  
644 uncertainties outlined in the text. **C:** Air-sea ammonia fluxes with latitude. Each box represents an  
645 air-sea flux calculated from observed concentration data. The vertical extent of the bars represents  
646 the range of possible flux values, based on the uncertainty in the measurement of the concentration  
647 and pH data. Horizontal extent represents the latitudinal range over which fluxes are integrated  
648 (corresponding to the range over which the corresponding atmospheric concentration measurement  
649 was made). **D:** Detail of air-sea ammonia fluxes, omitting the large negative value observed during  
650 cruise D267. In C and D negative flux values represent a flux into the ocean and positive values a  
651 flux out of the ocean. The darker horizontal lines represent the mean calculated fluxes.  
652

653 Figure 5. Sensitivity of air-sea flux direction to **A.** temperature ( $T$ ,  $^{\circ}\text{C}$ ), **B.** pH and **C.** salinity ( $S$ ,  
654 unitless), over ranges commonly observed in the surface ocean. In each case lines represent lines of  
655 zero flux under the following conditions for each plot: **A.**  $\text{pH}=8$ ,  $S=35$ ; **B.**  $T=15^{\circ}\text{C}$ ,  $S=35$ ; **C.**  
656  $T=15^{\circ}\text{C}$ ,  $\text{pH}=8$ . For each plot a 'concentration coordinate' above the equilibrium line for a given  
657 condition represents a downward flux and a coordinate below the line an upward flux. Note that as  
658 these graphs present lines of 'equilibrium' between gas phase  $\text{NH}_3$  and total seawater  $\text{NH}_x$ , they  
659 represent the  $T$ , pH and salinity variability of both the Henry's Law equilibrium and the ammonium-  
660 ammonia equilibrium.  
661

662 Figure 6. Field data from AMT14 and AMT17. Details as Figure 4.

663 Figure 7. Summary of all air-sea ammonia fluxes presented in this work.

664

665

665

**Table 1. Summary of research cruises undertaken.**

Cruise	Ship	Date	Region
PS211	RV Poseidon Institut für Meereskunde (now IFM- GEOMAR, Kiel), Germany	September 1995	NE Atlantic transect: Reykjavik to Lisbon 39 to 65 North, -32 to -10 East
S18/01	RV Scotia Fisheries Research Services, Aberdeen, UK	December 2001	Northern North Sea (survey) 57.5 to 63 North, -6 to 5.5 East
JR75	RRS James Clark Ross British Antarctic Survey, Cambridge, UK	June - July 2002	Arctic Ocean / Norwegian Sea (survey) 58.5 to 81.5 North, -7 to 13.5 East
D267	RRS Discovery Natural Environment Research Council, UK	November - December 2002	Irminger Basin / NE Atlantic (survey) 52.5 to 65.5 North, -35.5 to -6 East
AMT14	RRS Discovery Natural Environment Research Council, UK	April - June 2004	Atlantic Meridional Transect (AMT): Falklands to UK -37 to 49 North, -36 to -6 East
AMT17	RRS Discovery Natural Environment Research Council, UK	October - November 2005	Atlantic Meridional Transect (AMT): UK to Cape Town -36 to 56 North, -39 to 19 East

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**Table 2. Summary of methods used and personnel involved in sampling, sample preparation and analysis during and after the 6 cruises considered in this paper. Method details are outlined in Sections 2.1 to 2.2.**

Cruise	Seawater method	Operator	Atmospheric Method	Operator(s)	pH method	Operator
PS211	FIGD-IC	S. W. Gibb	Filter pack (analysis by FIGD-IC)	S. W. Gibb	n/a	n/a
S18/01	Manual OPA	M. T. Johnson	Filter pack (OPA analysis)	M. T. Johnson	Calibrated electrode	M. T. Johnson
JR75	Manual OPA	M. T. Johnson	Filter pack (OPA)	M. T. Johnson	Calibrated electrode	M. T. Johnson
D267	Manual OPA	M. T. Johnson	Filter pack (OPA)	M. T. Johnson	Calibrated electrode	M. T. Johnson
AMT14	Manual OPA	S.Painter (NOC)	Filter pack (OPA)	K. Biswas, and T. G. Bell	Calculation from CO <sub>2</sub> system parameters	A. W. Hind
AMT17	Automated OPA	E. M. S. Woodward	Filter pack (Manual OPA)	T. Lesworth	n/a	n/a

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**Table 3. Summary of data from the four high latitude cruises presented here, along with previous studies in similar regions for comparison. Data in parentheses are mean measured concentrations during each cruise / previous study.**

<b>Cruise</b>	<b>Region</b>	<b>Season</b>	<b>(NH<sub>3(g)</sub>) nmol m<sup>-3</sup></b>	<b>Surface [NH<sub>x</sub>(sw)] nM</b>
PS211	NE Atlantic	Autumn	1.4-8.0 (4.5)	90-450 (286) <i>stdev</i> =87
S18/01	Northern North Sea	Winter	1.4-5.5 (2.9)	30-218 (72) <i>stdev</i> =51
JR75	Norwegian Sea / Arctic Ocean	Spring-Summer	1.4-15.9 (7.5)	29-616 (146) <i>stdev</i> =142
D267	Irminger Basin	Winter	5.5-25.8 (n=2)	17-217 (101) <i>stdev</i> =95.7
<b>Other studies</b>	<b>Region</b>	<b>Season</b>	<b>(NH<sub>3(g)</sub>) nmol m<sup>-3</sup></b>	<b>[NH<sub>x</sub>(sw)] nM</b>
<i>Johnson et al.</i> , [2007]	NE Atlantic	Spring	-	47-742 (266) <i>stdev</i> =203
<i>Rees et al.</i> , [2002]	Northern North Sea	Spring	-	30-70 (50)
<i>Rees et al.</i> , [2001]	Oligotrophic NE Atlantic (<50°N)	Summer	-	55-110 (80)
<i>Asman et al.</i> , [1994]	Southern North Sea	February - October	2 - 88	300-4300 (~1000)
<i>Harrison et al.</i> , [1993]	NW Atlantic	Spring	-	80-300
<i>Ottley and Harrison</i> [1993]	Southern North Sea		3-	
<i>Edmunds</i> [1991]	Southern North Sea	Annual coverage	-	<500-32000 (1500)

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**Table 4. Summary of data from the two AMT transect cruises presented here, along with previous studies in similar regions for comparison. Concentration data in parentheses are mean measured values for each cruise / previous study except in the data of *Norman and Leck* [2005], where *median* values are presented.**

<b>Cruise</b>	<b>Region</b>	<b>(NH<sub>3(g)</sub>) nmol m<sup>-3</sup></b>	<b>Surface [NH<sub>x(sw)</sub>] nM</b>
AMT14	Atlantic (transect S-N)	1.3-7.6 (4.3) <i>stdev 1.83</i>	2-376 (69) <i>stdev 88</i>
AMT17	Atlantic (transect N-S)	0.02-1.0 (0.2) <i>stdev 0.2</i>	2-83 (13) <i>stdev 15.33</i>
<b>Other studies</b>	<b>Region</b>	<b>(NH<sub>3(g)</sub>) nmol m<sup>-3</sup></b>	<b>Surface [NH<sub>x(sw)</sub>] nM</b>
<i>Ayers and Gras</i> [1980]	Southern Ocean (Cape Grim)	0.6 - 6.0 (3.5)	-
<i>Lebel et al.</i> , [1985]	Bermuda	20	-
<i>Le Bouteiller</i> [1986]	Equatorial Atlantic	-	<50
<i>Brzezinski</i> [1988]	Tropic Atlantic	-	<3 - 160
<i>Glibert et al.</i> , [1988]	Sargasso	-	<30
<i>Longhurst et al.</i> , [1989]	Sargasso	-	90 +/- 65
<i>Quinn et al.</i> , [1990]	Central Pacific	0.01 - 3.4 (0.67)	400 +/- 300
<i>Quinn et al.</i> , [1996]	Bermuda	-	10 - 200
<i>Gibb et al.</i> , [1999]	Arabian Sea:		
	Coastal	2.5 – 5.6 (3.8)	80 – 250 (130)
	Remote	0.4 – 1.8 (1.0)	70 – 230 (190)
<i>McKee</i> [2001]	Atlantic transect (AMT 9 )	0.7 - 4.2 (1.9)	<40
<i>Norman and Leck</i> [2005]	Central Atlantic (15 °N – 5 °S)	3.7 – 18.4 (9.7)	-
	Southern Atlantic (5 °S – 35 °S)	0.1 – 7.7 (2.1)	-
	Southern Indian Ocean (35 °S – 26 °S)	0.3 – 2.1 (1.1)	-
	Central Indian Ocean (26 °S – 15 °S)	0.05 – 0.2 (0.1)	-

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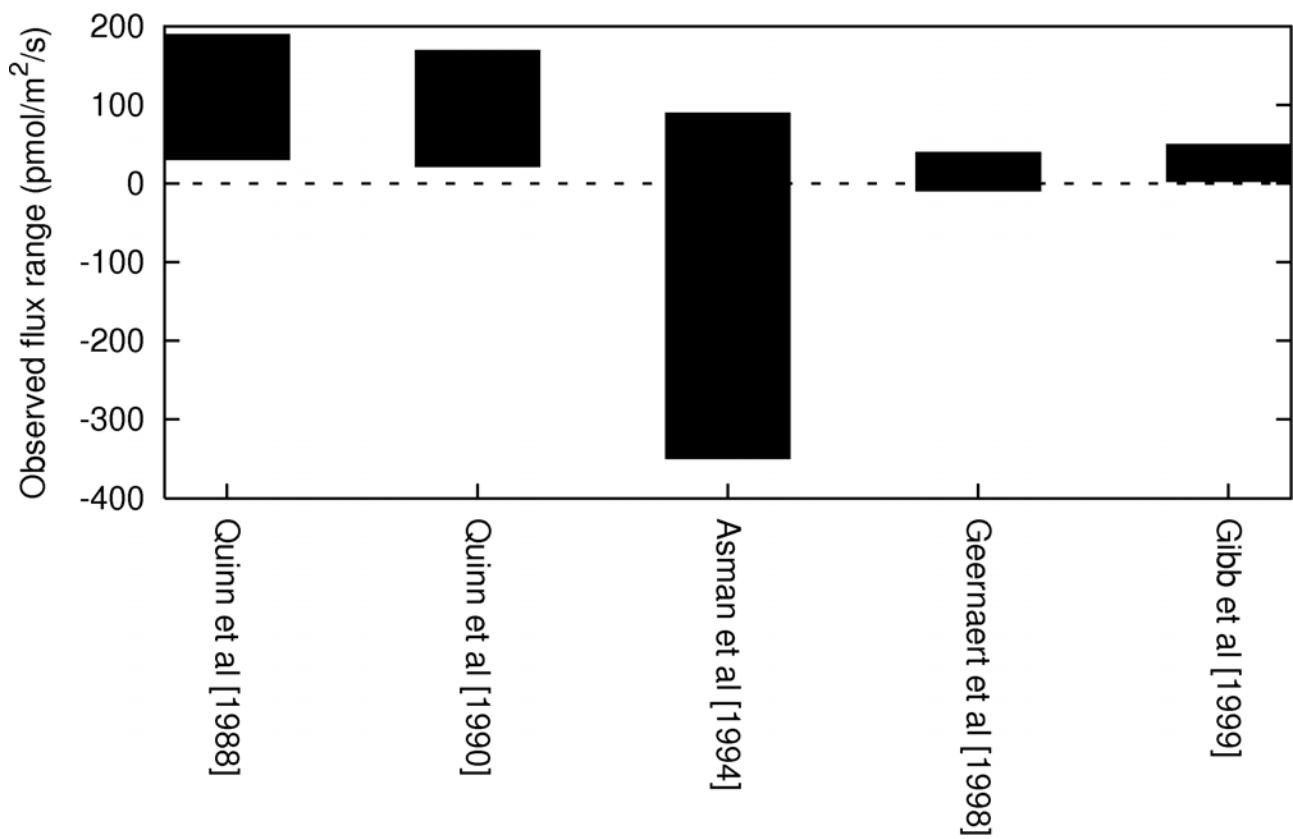
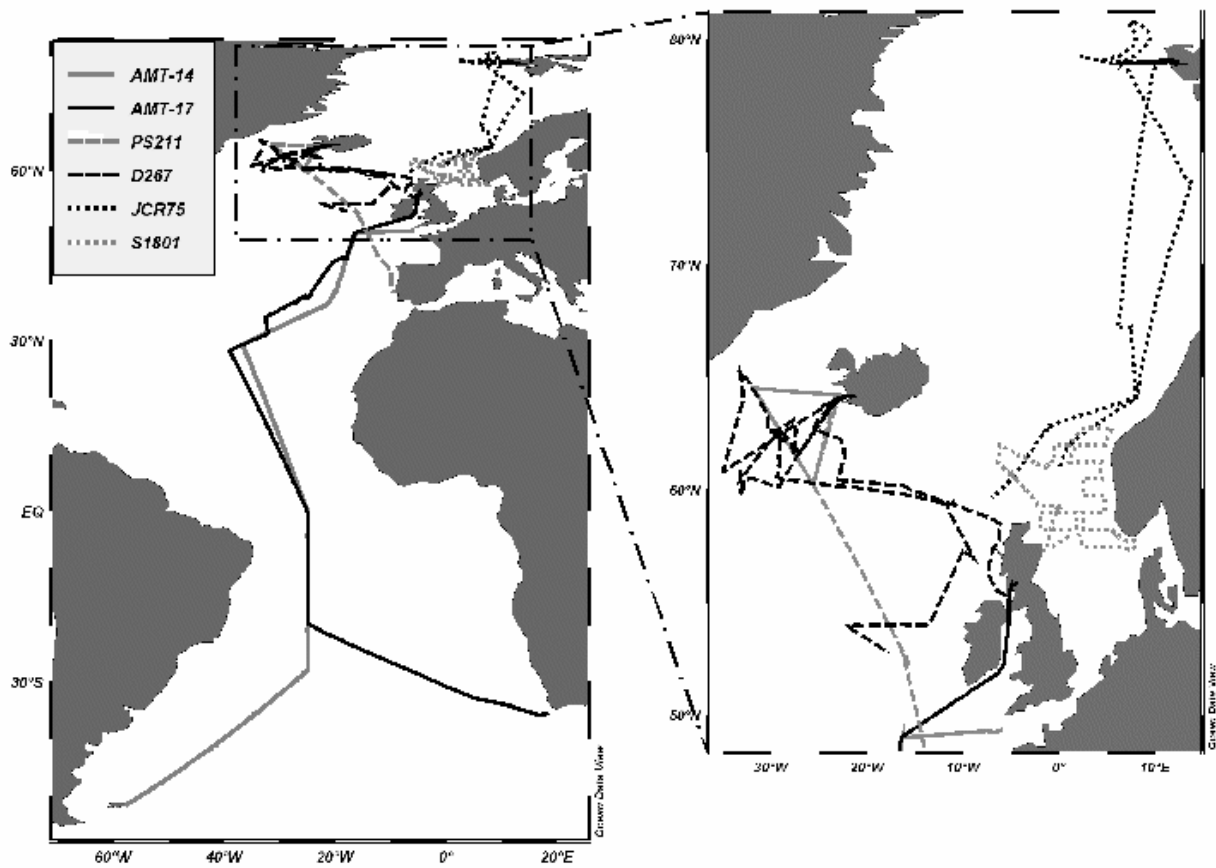


Figure 1: Summary of data presented by previous studies of air-sea ammonia flux. Only data from simultaneous measurements of seawater and gas phase species is considered. Note positive values represent fluxes from sea to air (i.e. emission).



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 680 *Figure 2. Tracks of the 6 cruises from which data is presented. Table 1 provides further details. Plot*  
 681 *produced using the freely-available **Ocean Data View** (<http://odv.awi-bremerhaven.de/home.html>).*

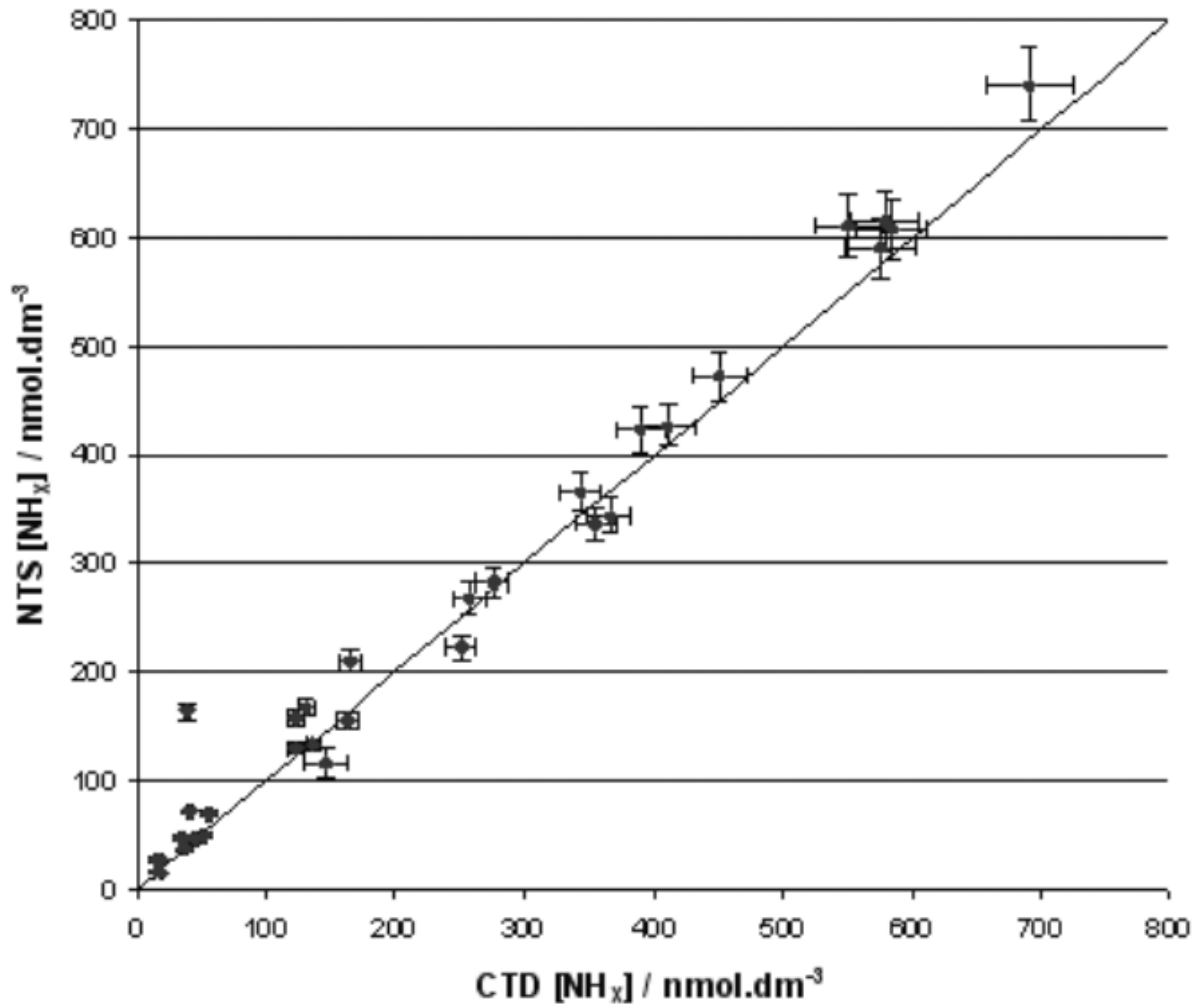


Figure 3: Comparison of simultaneous measurements of NTS (non-toxic supply) and CTD (Niskin)  $\text{NH}_x$  concentration from cruises S18/01, JR75 and D267. Error bars represent approximately 95% confidence limits in the measured data. No such comparable data were available for the remaining cruises.

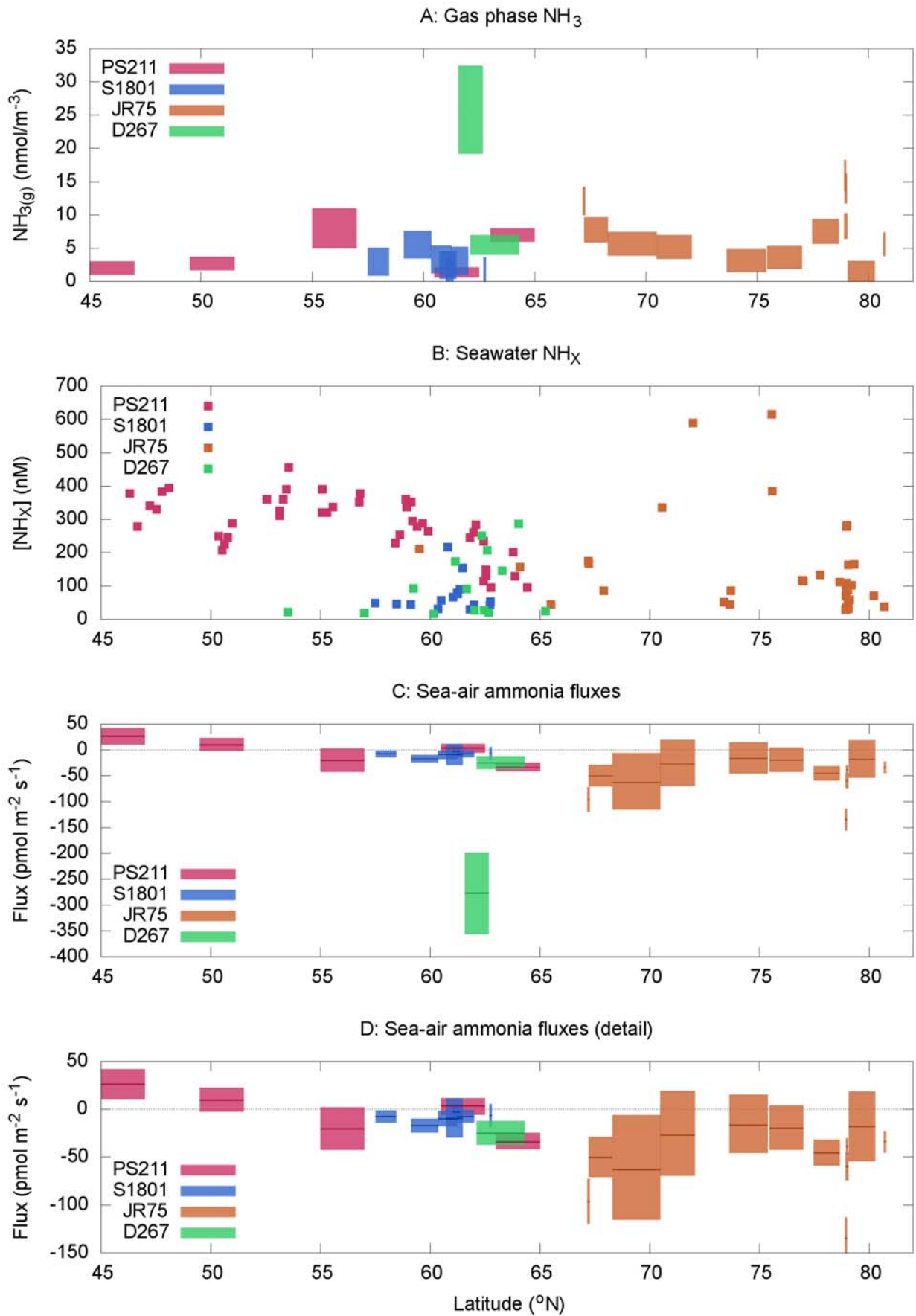
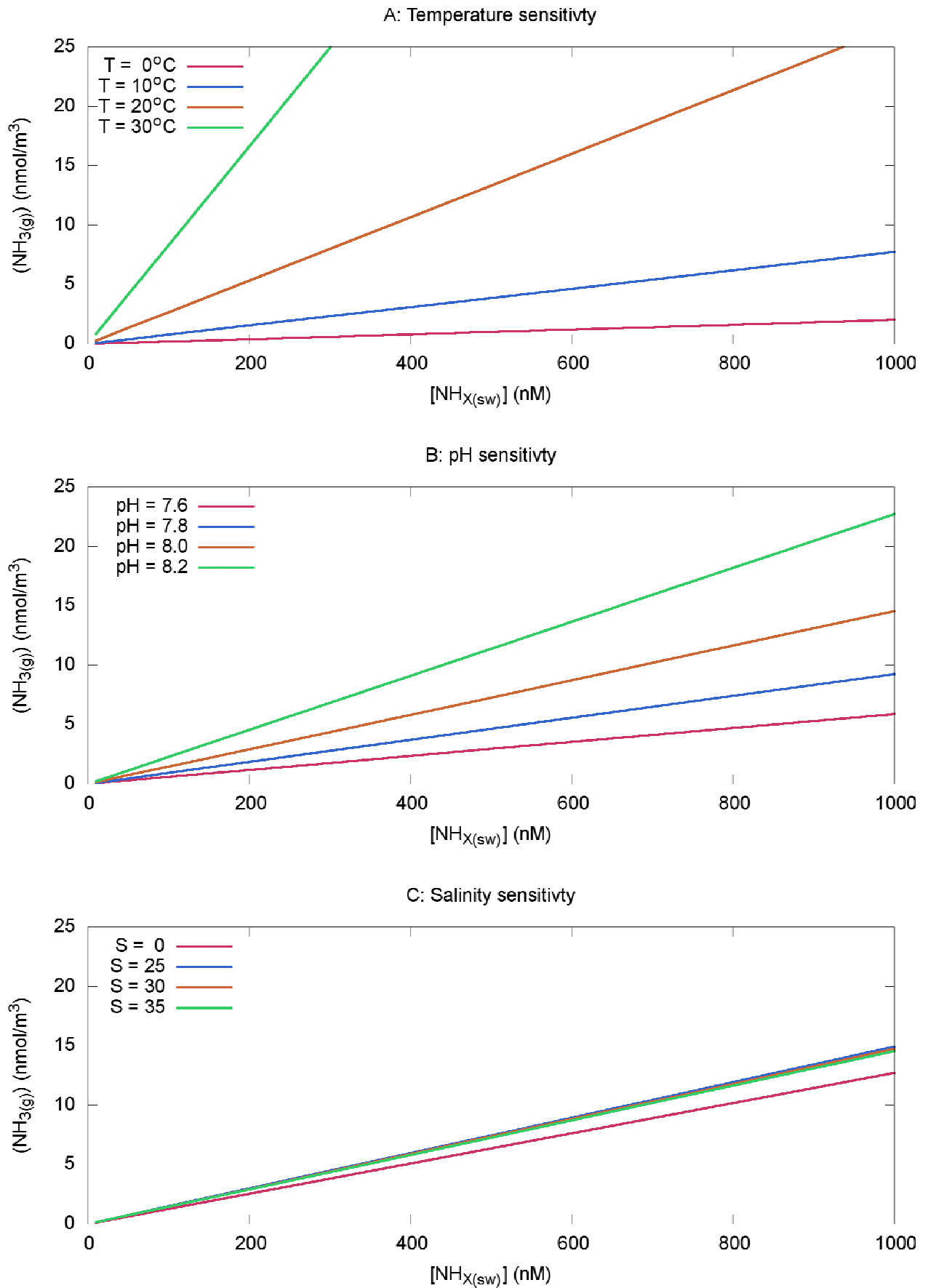


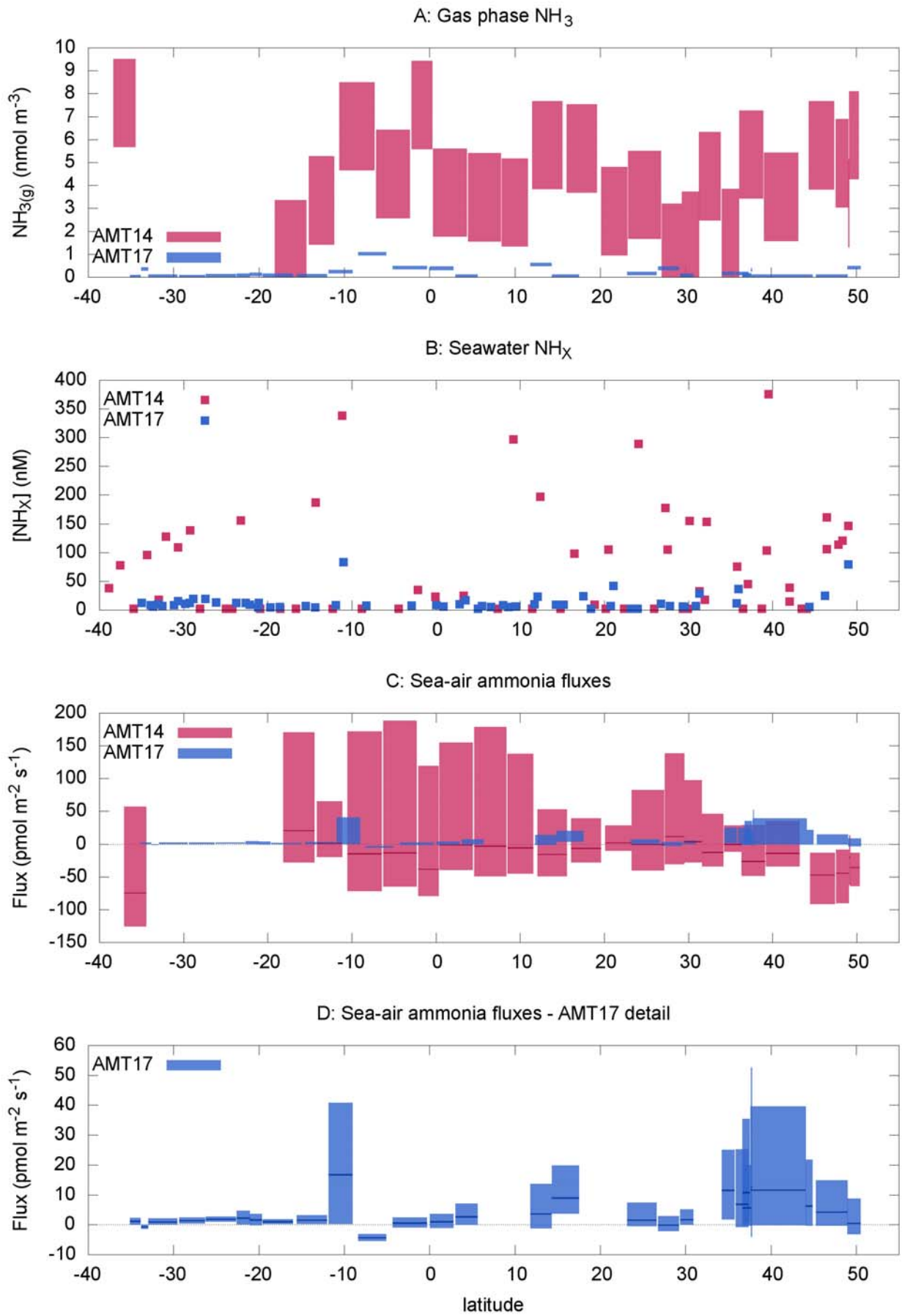
Figure 4: Data from the high latitude cruises conducted during this study. A: Gas phase data; vertical extent of each box corresponds to uncertainty in measurement at an approximate 95%

confidence interval. Horizontal extent represents the latitudinal range over which samples were collected. **B**: Surface seawater ammonium concentration; For simplicity, error bars are not presented on these data, as the uncertainty is negligible in air-sea flux calculation relative to the other uncertainties outlined in the text. **C**: Air-sea ammonia fluxes with latitude. Each box represents an air-sea flux calculated from observed concentration data. The vertical extent of the bars represents the range of possible flux values, based on the uncertainty in the measurement of the concentration and pH data. Horizontal extent represents the latitudinal range over which fluxes are integrated (corresponding to the range over which the corresponding atmospheric concentration measurement was made). **D**: Detail of air-sea ammonia fluxes, omitting the large negative value observed during cruise D267. In C and D negative flux values represent a flux into the ocean and positive values a flux out of the ocean. The darker horizontal lines represent the mean calculated fluxes.

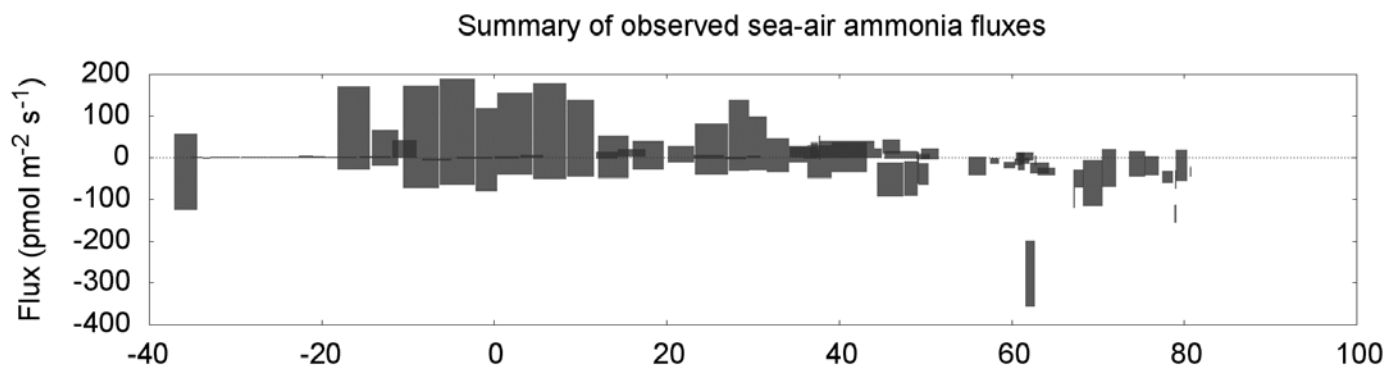


684 Figure 5. Sensitivity of air-sea flux direction to **A.** temperature (T, °C), **B.** pH and **C.** salinity (S,  
 685 unitless), over ranges commonly observed in the surface ocean. In each case lines represent lines of

686 zero flux under the following conditions for each plot: **A.** pH=8, S=35; **B.** T=15°C, S=35; **C.**  
687 T=15°C, pH=8. For each plot a 'concentration coordinate' above the equilibrium line for a given  
688 condition represents a downward flux and a coordinate below the line an upward flux. Note that as  
689 these graphs present lines of 'equilibrium' between gas phase NH<sub>3</sub> and total seawater NH<sub>x</sub>, they  
690 represent the T, pH and salinity variability of both the Henry's Law equilibrium and the ammonium-  
691 ammonia equilibrium.



692 Figure 6. Field data from AMT14 and AMT17. Details as Figure 4.



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694 Figure 7. Summary of all air-sea ammonia fluxes presented in this work.