DETERMINATION OF ATMOSPHERIC MERCURY DURING THE NORTH SEA EXPERIMENT

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Abstract. Total gaseous mercury (TGM) and rainwater were collected on board of two research vessels (F. S. ALKOR and R.V. BELGICA) positioned 200 km apart in the center of the North Sea during the North Sea Experiment, September 1991. On the F. S. ALKOR (up-wind ship) TGM concentrations ranged from 0.7 to 2.6 $ng \cdot m^{-3}$ with an average of 1.5 $ng \cdot m^{-3}$ and on the R. V. BELGICA (down-wind ship) TGM ranged from 0.7 to 1.9 $ng \cdot m^{-3}$ with an average of 1.2 $ng \cdot m^{-3}$. An average 20% decrease is observed from the up-wind to the down-wind ship, which may largely be affected by entrainment into the free troposphere. An overall removal (entrainment) velocity of 0.95 $cm \cdot s^{-1}$ was calculated for the whole experiment. The average removal velocity was 0.5 $cm \cdot s^{-1}$ for dry periods and varied between 1 to 5 $cm \cdot s^{-1}$ during rain events. Rainwater concentrations varied between 5 and 25 $ng \cdot l^{-1}$. Based on these data an annual wet deposition flux of 1.08 ng Hg cm^{-2} yr^{-1} was estimated for the North Sea.

keywords: mercury, atmosphere, rainwater, marine

1. Introduction

The North Sea Experiment (NOSE 1991) was carried out from September 15 to 27, 1991 as part of the EUROTRAC "Air-Sea Exchange (ASE)" project. The North Sea is a relatively enclosed body of water receiving inputs from large areas of industrialized Northern Europe. Due to its location and economic significance, there is much international concern over pollutant inputs to the North Sea. There is strong evidence that atmospheric pollutants emitted over Europe, are significantly removed into regional and coastal waters. For many pollutants, atmospheric deposition provides a major input pathway, in some cases exceeding inputs from rivers and direct coastal discharges. In order to measure changes in concentrations of trace metals, sulfur- and nitrogen compounds in air and precipitation in a moving air mass (Lagrangian experiment), samples were collected on board of two research vessels arranged to lie 200 km apart, aligned in wind and along air-parcel forward trajectories. In a Lagrangian experiment the same air mass parcel is sampled at different time intervals. Variations in concentrations of a given component during transport are thus either due to internal processes (such as oxidation or adsorption on particles) or external processes such as sources or sinks. Whereas over land anthropogenic activities represent a variety of atmospheric emission sources, over sea only natural emission sources, which are much more homogeneous than over land, need to be considered. Fluxes can thus be derived using a mass balance box- model approach. The aim of the Hg investigation during this experiment was to obtain more information about (1) the atmospheric Hg concentrations above the North Sea and (2) the processes that may affect these concentrations.

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2. Methods and Materials

2.1 SAMPLING STRATEGY

Ambient air and rainwater samples were collected for Hg analysis by the Free University of Brussels (VUB), Belgium on board of the R. V. BELGICA and by the GKSS Research Center Geesthacht, Germany on board of the F. S. ALKOR. The two ships were positioned on a circle with a diameter of 200 km of which the center was placed at 55° 5'N and 4°0'E (Figure 1). The two research vessels were aligned in wind direction with the F. S. ALKOR always upwind of the R. V. BELGICA. Sampling on the R.V. BELGICA was delayed according to the calculated air mass travel time, based on the actual wind speed of the ships. A wind speed of 10 $m \cdot s^{-1}$ and a distance of 200 km resulted in a transport time of 5.5 h by which the downwind ship had to delay its sampling interval. Every 8 h new positions were taken on the circle. Forecasted trajectories were received on the F.S. Alkor up to four times a day from the UK Meteorological Office and these, together with synoptic weather charts, were used to position the ships and coordinate sampling operations. Once the position had been taken, ships moved slowly into the wind for undisturbed sampling conditions. Sampling was stopped during the travel time between positions. Samplers were installed on the top bridge of the ship, away from possible sources of contamination (chimney stacks, etc.).

Meteorological data were collected continuously throughout the whole experiment on both ships. In cooperation with the German Meteorological Service weather balloons were released twice daily from the F. S. ALKOR to provide information on upper air mass structures.

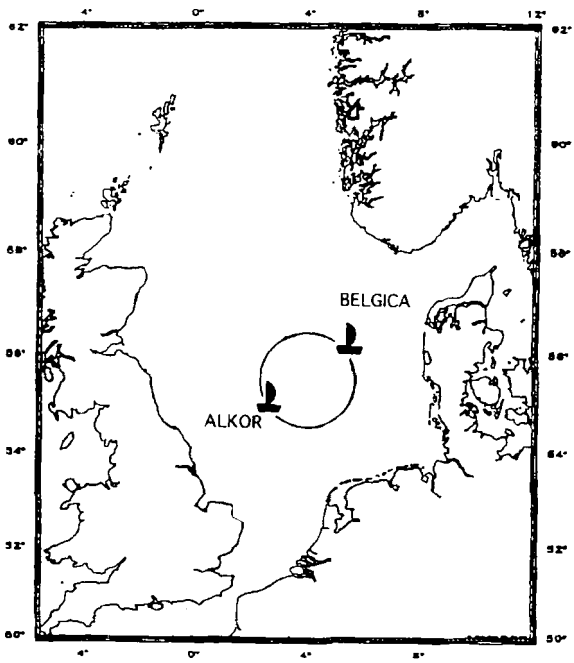

Fig 1. Position of the ships during the North Sea Experiment, September 1991

2.2 ANALYTICAL METHODS

TGM was sampled by the Free University of Brussels using three gold traps placed in line. The gold traps were quartz tubes filled with 3.5 cm of gold coated sand. A quartz fiber filter was placed in front of the first gold column. Sampling was performed at a flow rate of 20 L/hour and volumes sampled ranged from 150 to 500 L. The measurements of the gold columns were performed on board of the ship using a two stage gold amalgamation atomic fluorescence technique (Fitzgerald and Gill, 1979; Baeyens, 1992). Calibration was performed by injecting Hg saturated air onto the analytical column. All sampling was performed using duplicate sampling trains.

TGM was sampled by GKSS on gold coated glass beads. Two quartz tubes, 0.1 cm in diameter, were filled with 1.5 cm glass beads. A third tube filled with a gold/platinum gauze is placed between the adsorber tubes and a pump to prevent contamination. Ambient air was sucked through a 0.5 cm quartz wool plug before passing through the adsorber tubes. Approximately 500 L was air was collected with flow rates of 50 L/hour. To prevent contamination during storage 10 g of silver wool was kept in the container to bind gaseous Hg diffusing into the container. The analysis was carried out at GKSS using a two stage gold amalgamation atomic fluorescence technique as described above. For both laboratories the reproducibility of duplicate sampling trains is better than 5%.

Rainwater was collected on an event basis. The Free University of Brussels used a 22.5 cm diameter PTFE funnel and thoroughly cleaned FEP bottles. After sampling the rainwater was acidified with 1 ml HCl (Merck, suprapur)/100 ml of sample. Between rain events the funnel was rinsed with Milli-Q water and stored double bagged. A funnel blank was taken between each rain event. Total Hg measurements were performed in the lab. The sample was oxidized with 1% BrCl and analysis was performed using the cold vapor atomic fluorescence technique gold amalgamation preconcentration using $SnCl_2$ as a reducing agent (Bloom and Crecelius, 1983).

GKSS Research Center used a 35 cm diameter PTFE funnel and thoroughly cleaned borosilicate glass bottles. Samples were acidified with 1ml HCl/100 ml sample and analyzed with the same procedure as described above.

3. Results and Discussion

3.1 METEOROLOGICAL CONDITIONS

Throughout the whole experiment the prevailing winds were westerly at a wind speed of 10-15 $m \cdot s^{-1}$, except from September 20 to 22 and in the beginning of the experiment. Around September 20 a high pressure system developed briefly over the area with reduced wind speeds, southerly winds and reduction in the mixing height from 1000m to less than 500m (Figure 2, samples 12 to 15). This atmospheric pattern was disrupted by the passage of a front on 22 September with an associated rain event and return to westerly winds. This was the largest rain event observed with an average rainfall of 5mm (samples 15 to 21).

3.2. TOTAL GASEOUS Hg

Comparison of TGM concentrations between the F.S. ALKOR and R. V. BELGICA, together with the wind direction and wind speed is shown in Figure 2. TGM varied from 0.7 to 2.6 ng·m^{-3} with an average concentration of 1.5 ng·m^{-3} on the F.S. ALKOR (up-wind ship) while TGM varied from 0.7 to 1.9 ng·m^{-3} with an average of 1.2 ng·m^{-3} on the R.V. BELGICA (down-wind ship). These average concentrations are lower than previously reported data for the Northern Hemisphere (Slemr,1992; Fitzgerald *et al.*., 1983; Schroeder, 1994) but are consistent with our measurements on the North Sea Platform and on the Island of Sylt in 1991 and 1992 (Ebinghaus *et al.*, 1994). On two occasions concentrations lower than 1 ng·m^{-3} were recorded on both ships (intervals 4 and 13) whereas no breakthrough of Hg was detected on any of the samples. The largest difference between the two ships was observed on sampling interval 18, corresponding to the largest difference in observed wind direction between the two ships. The more southerly winds (samples 12 to 16) did not give rise to increased TGM concentrations.

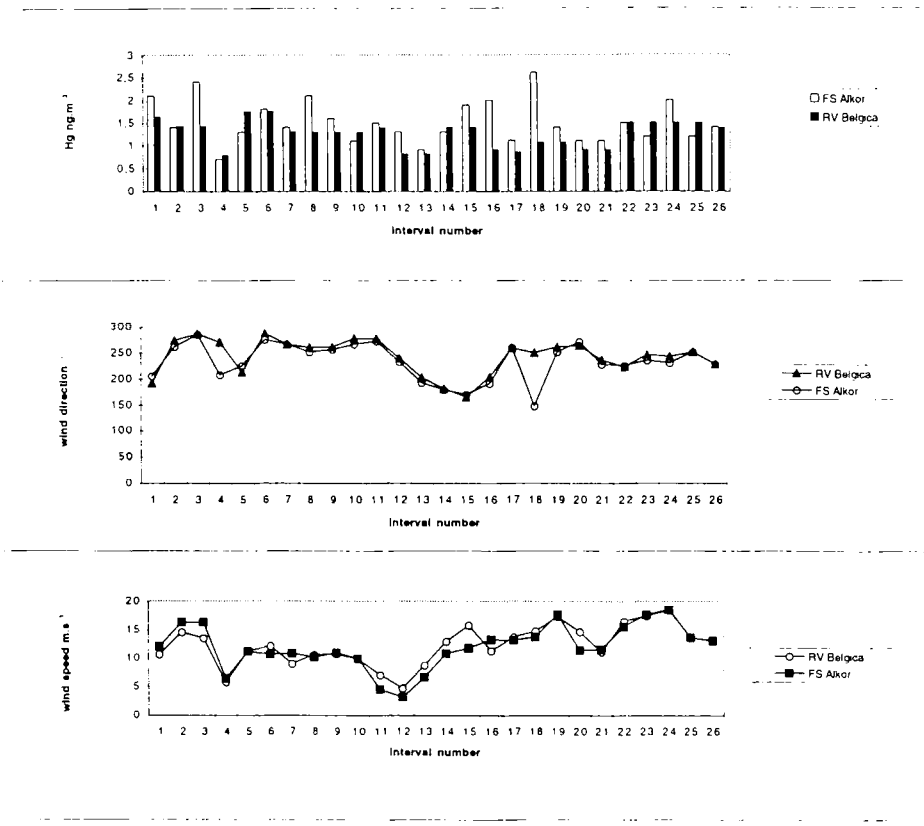

Fig 2. Total gaseous Hg concentrations (TGM), wind direction and wind speed measured on the F.S ALKOR (up-wind ship) and R.V. BELGICA (down-wind ship)

An average 20% decrease in TGM from the up-wind to the down-wind ship was found. A substantial decrease in almost all trace metal concentrations on size segregated aerosols from the up-wind to down-wind ship was found (Schulz *et al.*, 1994, Francois *et al.*, 1992, Injuk et al., 1992) as well as a substantial decrease in concentrations of gaseous nitrogen compounds (Harrison *et al.*, 1994, Larsen, 1994). The 30-40% decrease which was found for anthropogenic elements, was much larger than could be expected for dry deposition alone. Important factors which may influence changes in concentrations in chemical compounds during the transport of air between the ships can arise from (1) entrainment with the free troposphere by vertical dilution, (2) chemical transformation, (3) rainfall scavenging and (4) air-sea exchange.

Entrainment in the free troposphere is probably the dominating reason for the depletion in the boundary layer. An overall removal velocity ($vr = -\ln(Clee/Cluff)\, zi/\Delta t$) can be calculated, where Clee and Cluff are the Hg concentrations on down-wind and upwind ships, zi is the mixing layer height and Δt is the travel time of the air mass. Mixing layer heights were inferred from radiosonde data (Schulz and Larsen, 1992) and vary between 200 and 1400m. Calculated removal velocities varied between 0 and 5.5 $cm \cdot s^{-1}$ with an average of 0.95 $cm \cdot s^{-1}$ for the whole experiment. The average removal velocity for dry periods is 0.5 $cm \cdot s^{-1}$, whereas during rain events the removal velocity varies between 1 and 5 $cm \cdot s^{-1}$. For nitrogen species entrainment velocities were estimated to be typically 1 to 2 $cm \cdot s^{-1}$ and up to 5 $cm \cdot s^{-1}$ or more during frontal passages (Larsen, 1994). During rain events oxidation of elemental mercury and rainfall scavenging may be responsible for the increased removal rates.

Concerning air-sea exchange, surface waters of the North Sea are generally supersaturated with dissolved gaseous Hg (Baeyens and Leermakers, 1996, Coquery and Cossa, 1995). An average evasion flux of 0.73 ng Hg cm^{-2} yr^{-1} was calculated for open waters of the North Sea whereas for coastal stations this evasion flux can reach 8 ng Hg cm^{-2} yr^{-1} (Baeyens and Leermakers, 1996). The calculated evasion flux is comparable in magnitude to the wet depositional flux (see further). However, is this experiment no dissolved gaseous Hg measurements were made and gaseous evasion could not be detected from the atmospheric measurements as the concentrations in the down-wind ship are in most cases lower than the up-wind ship. Based on an evasion flux of 0.73 ng Hg cm^{-2} yr^{-1} we calculated the expected increases in TGM between the F.S. ALKOR and the R.V. BELGICA for the 6 h time interval assuming a homogeneous concentration in the mixed layer and a mixing layer height of 1000m. This increase amounts to 0.003 $ng \cdot m^{-3}$ and is thus undetectable.

Hg concentrations in rainwater varied from 5 to 25 $ng \cdot L^{-1}$ and are comparable to data found in coastal and marine environments (Gill and Fitzgerald, 1987; Baeyens *et al.*, 1991; Mason *et al.*, 1992) and are consistent with our measurements on the North Sea Platform and on the Island of Sylt in 1991 and 1992. (Table I). Based on these data, wet deposition fluxes of Hg to the North Sea can be estimated. Using an average amount of precipitation over the North Sea of 685 mm (Salomons *et al.*, 1988), the wet deposition flux of Hg amounts to 1.08 ng Hg cm^{-2} yr^{1-}.

Table I. Hg concentrations in rainwater on the F. S. ALKOR and R. V. BELGICA

ALKOR			BELGICA			
Date	Time	Hg $ng \cdot l^{-1}$	Date	Time	Hg $ng \cdot l^{-1}$	Rainfall mm
			16.9.1991	13:30-22:30	24.7	1.2
22.9.1991	05:40-09:20	24.1	22.9.1991	02:20-07:45	21.9	3.4
			22-23.9.1991	09:25-14:00	4.9	1.8
24.9.1991	02:15-07:15	15.1	23-24.9.1991	22:00-07:30	11.9	1.6

4. Conclusions

TGM was measured on board of two research vessels positioned 200 km apart in the center of the North Sea in September 1991. The average concentrations of TGM measured on the R.V. BELGICA (1.2 $ng \cdot m^{-3}$) and on the F.S. ALKOR (1.5 $ng \cdot m^{-3}$) are lower than previously reported TGM concentrations for the Northern Hemisphere. An average 20% decrease was observed between the upwind and the downwind ship which may predominantly be due to tropospheric entrainment. An overall removal velocity of 0.95 $cm \cdot s^{-1}$ was calculated for the whole experiment. The average removal velocity was 0.5 $cm \cdot s^{-1}$ in dry periods and >1 $cm \cdot s^{-1}$ during rain events. The Lagrangian experiment did not permit to detect evasion of gaseous Hg from the surface waters as removal of gaseous Hg from the boundary layer dominates. Based on the average Hg concentrations in rainwater of 15.8 $ng \cdot L^{-1}$, a wet depositional flux of Hg to the North Sea of 1.08 ng Hg cm^{-2} yr^{1-} was calculated.

Acknowledgments

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