Ebinghaus, R.; Jennings, S.G.; Kock, H.H.; Derwent, R.G.; Manning, A.J.; Spain, T.G.:

Decreasing trends in total gaseous mercury observations in baseline air at Mace Head, Ireland from 1996 to 2009

In: Atmospheric Environment (2011) Elsevier

DOI: 10.1016/j.atmosenv.2011.01.033

Decreasing trends in total gaseous mercury in baseline air at Mace Head, Ireland from 1996 to 2009

R. Ebinghaus[a,*], S.G. Jennings[b], H.H. Kock[c], R.G. Derwent[d], A.J. Manning[e], T.G. Spain[b]

[a]*Institute of Coastal Research, Helmholtz-Zentrum Geesthacht, Germany*
[b]*School of Physics, National University of Ireland, Galway, Ireland*
[c]*rdscientific, Newbury, Berkshire, United Kingdom*
[d]*Met Office, Exeter, Devon, United Kingdom*

*corresponding author. Tel.: +49 4152 872354

E-mail address: ralf.ebinghaus@hzg.de

ABSTRACT

In this study, the concentrations of total gaseous mercury in air masses arriving at Mace Head, Ireland after having traversed the thousands of kilometres uninterrupted fetch of the North Atlantic Ocean have been measured and evaluated for the time period January 1996 to December 2009. Hourly attribution of air mass origins has been conducted to understand the sources that contribute to the observed levels at Mace Head and to separate baseline air masses, representing Northern hemispheric background concentration. Over a 14-year period, a statistically significant negative (downwards) trend of -0.028 ± 0.01 ng m^{-3} yr^{-1}, representing a trend of 1.6 – 2.0% per year, has been detected in the total gaseous mercury levels in these baseline air masses. These findings are set in the context of the available literature studies of atmospheric Hg trends.

Keywords: **total gaseous mercury, long term trends, Mace Head, Hg**

1. Introduction

Mercury (Hg) is emitted into the atmosphere from a variety of anthropogenic and natural sources. Of the anthropogenic sources, among the most important are fossil

fuel combustion, smelting, cement production and waste incineration, while the oceans are the largest natural source of Hg to the atmosphere, volcanism also makes an important contribution (Pirrone et al., 1996; 2009; Ferrara et al., 2000; Mason 2009, Pacyna et al., 2006; 2010). It has been suggested that due to intensified anthropogenic emissions of mercury since the beginning of the industrialization the global atmospheric burden has increased over the past 150 years.

Evidence of long-term changes in the atmospheric mercury burden have been derived from chemical analysis of lake sediments, ice cores, peat deposits and firn air records (Pirrone et al. 1998; Bindler et al., 2001; Biester et al., 2002; Lindberg et al., 2007; Fain et al., 2009). These studies identify a peak in the atmospheric mercury concentration during the 1970's in the Northern Hemisphere. A growing number of these records from both hemispheres demonstrate an approximate threefold increase of mercury deposition since pre-industrial times (Lindberg et al., 2007). Intensive efforts have been undertaken especially in Europe and North America to reduce mercury emissions and harmful effects of this toxic element on humans and ecosystems. This reduction however is believed to be compensated or even surpassed by strongly increasing emissions in rapidly industrialising countries (Pacyna et al, 2010; Streets and Zhang, 2009).

In principle, any change in the global atmospheric burden should be reflected in atmospheric baseline concentrations. Because the first reliable measurement data were published only 3 decades ago, it is extremely difficult to derive a multi-decadal global trend estimate based on the available spatially and temporally incomplete air concentration data. In 1995, Fitzgerald (1995) argued for and defined the basic

requirements of a global atmospheric mercury network. This has partly been accomplished on a regional scale in Canada and the U.S. (CAMNet and AMNet). In November 2010, a European initiative with a global perspective has been started (Global Mercury Observation System, GMOS; www.gmos.eu)

Nevertheless, although the number of atmospheric Hg monitoring stations has increased (Kim et al., 2005), the database is sparse, especially in remote locations.

The Mace Head dataset comprises the longest existing time series of atmospheric mercury measurements with high time resolution in the temperate marine background atmosphere. The measurements started in September 1995, sometime after the Alert station began making mercury observations in Arctic Canada. Here, three-hourly attribution of air mass origins has been conducted to understand the sources that contribute to the observed levels at Mace Head. Classification of air masses can be done by support measurements such as ^{222}Radon (Brunke et al., 2009) or by meteorological analysis (Manning et al., 2003, 2010). Total gaseous mercury (TGM) baseline concentrations at Mace Head have been estimated for the 14 years measurement period between January 1996 and December 2009, based on hourly concentration averages using meteorological analyses and a Lagrangian dispersion model, as described below. These baseline data are considered to be representative for the well-mixed mid-latitude Northern Hemisphere air masses that have had no recent influence from man-made emissions over the previous 12 days. They have been used to determine trends in the TGM concentrations over the 1996 – 2009 period.

2. Methods

2.1 Sampling site

Mace Head is located in County Galway near Carna on the west coast of Ireland at 53°20'N; 9°54'W. It is exposed to the North Atlantic Ocean having a wide clean sector between 180° and 300°. It is ideally situated to study atmospheric composition under Northern Atlantic hemispheric background conditions and also under regionally-polluted European continental conditions, when air masses are originating from an easterly direction (Jennings et al., 1993; Oltmans and Levy, 1994; Ebinghaus et al., 1995). The meteorological records show that, on average, over 50% of the air masses arriving at Mace Head are within the clean sector and have recently traversed the thousands of kilometres of uninterrupted fetch across the North Atlantic Ocean. The climate at Mace Head is classified as maritime. There is no industrial activity which would influence measurements at the station within about 90 km of the site and the nearest major conurbation of Galway city is located 90 km east of Mace Head.

2.2 Instrumentation

The major techniques applied for highly-time resolved mercury measurements in ambient air are the automated atomic fluorescence (AFS) analyzer () and the automated atomic absorption (AAS) analyzer (Schroeder et al.,1995; Urba et al., 1995). Because of the extremely low concentrations at which Hg species normally exist in the atmosphere, both techniques involve a pre-concentration step (amalgamation with gold). In the remote atmosphere the TGM fraction consists of gaseous elemental mercury (GEM), the dominant compound by far, and the operationally defined reactive gaseous mercury (RGM) present in much lower

concentrations. Beside GEM and RGM, other volatile organic mercury species, such as dimethylmercury and monomethylmercurychloride can also interact with gold absorbers. Munthe et al. (2003) have shown that average concentrations of monomethylmercurychloride at Mace Head are 2 pg m^{-3} and consequently negligible for the TGM determination. The automated dual channel, single amalgamation, cold vapor atomic fluorescence analyzer in operation at Mace Head (Tekran-Analyzer Model 2537 A, Tekran Inc., Toronto, Canada) is capable of measuring TGM concentrations, even at baseline locations, with a minimum temporal resolution of 5 min. This instrument is referred to as the Tekran-Analyzer throughout this paper. The instrument features two gold cartridges. While one is adsorbing mercury during a sampling period the other is being thermally desorbed and is subsequently analyzed for TGM. The functions of each cartridge are then reversed, allowing continuous sampling of the incoming air stream. A 45 mm diameter Teflon pre-filter (pore size 0:2 mm) protects the sampling cartridges against contamination by particulate matter. The amalgamated mercury is thermally desorbed into an Argon carrier gas stream and analyzed using cold vapor atomic fluorescence spectroscopy (CVAFS). A detection limit of the order of 0,3 ng Hg m^{-3} can be achieved under these conditions.

The Tekran-Analyzer is equipped with an internal permeation source so that the instrument can be automatically calibrated. The instrument was connected to a PC that records the serial output data.

2.3 Quality assurance

The accuracy and precision of the applied instrumentation has been assessed through comparisons with commonly used manual methods at an urban/industrial site in Windsor, Ontario, Canada (Schroeder et al., 1995), at a remote site in Tuscany, Italy (Munthe et al., 2001) as well as at Mace Head (Ebinghaus et al., 1999) showing good agreement between the different techniques. The intercomparison exercise conducted at Mace Head in September 1995 marks the starting point of the long-term measurements reported here. Hg monitoring at Mace Head started immediately after completion of the field intercomparison exercise at the same location.

At Mace Head, the Tekran Analyzer routinely undergoes automated periodic re-calibrations every 25 h using the internal permeation source. Two point calibrations (zero and span) are performed separately for each cartridge. The internal permeation tube provides approximately 1 pg s^{-1} at 50^{o}C: Manual injections were used to initially calibrate the permeation device against a saturated mercury vapor standard. The adjustment of the permeation rate for drift correction is of the order of 1% per year over the entire measurement period.

Additionally, the instrument was calibrated approximately every three months (with a portable mercury source, Tekran, Model 2505) by manual injections of 8 µl of Hg saturated air with a gas tight syringe at defined temperatures. Fundamental work on this calibration technique has been carried out by Braman and Johnson (1974), Dumarey et al. (1985), Fitzgerald and Gill (1979) and others. In each case, the critical values obtained from a t-table at p = 95% and the particular degrees of freedom are larger than the calculated t-value of the mean from the measured TGM concentrations. There are no significant differences between the theoretical and the measured values.

2.4 Analysis of Mace Head total gaseous mercury observations

To determine trends in total gaseous mercury (TGM) observations it is important to select air masses that are representative of the well-mixed mid-latitude Northern Hemispheric marine boundary layer. The TGM levels monitored in these air masses are referred to as baseline levels and by definition they should have not been influenced by recent, local or regional emissions over the last 12 days. Over the period of the continuous trace gas observations at Mace Head, we have developed a number of methods to assign trace gas mixing ratios to specific air mass origins (Simmonds et al., 1997). In this study, to provide consistent air mass assignments over the entire study period, only the atmospheric dispersion modelling method has been employed.

The atmospheric dispersion modelling method employed the NAME (Numerical Atmospheric dispersion Modelling Environment) Lagrangian dispersion model (Ryall et al., 1998). The NAME model uses three-hourly three-dimensional meteorological fields from complex numerical meteorological weather prediction models to move abstract air parcels around a model domain. The three-dimensional model flow is interpolated to each particle location at each 15-minute time step. Using a random walk technique, each particle moves under the influence of the mean flow, wind meander and sub-grid scale turbulence. The random walk scheme uses velocity variance and Lagrangian timescale profiles determined from empirical fits to observational data to simulate the turbulent motion and are described in greater detail in Ryall and Maryon (1998) and Ryall et al. (1998). The model has been further

184 refined using a back-attribution technique (Manning et al., 2003, 2010). The NAME
185 model was run in backwards mode to estimate the impact of surface sources (assumed
186 within 100m of the ground) within 12 days of travel en-route to Mace Head. The
187 computational domain covered 100^{o} W to 45.125^{o} E and 10^{o}N to 80.125^{o}N and
188 extended to more than 10 km vertically. For each 3-hour period, 33000 inert model
189 particles were used to describe the atmospheric dispersion. Baseline concentrations
190 are defined as those that have not been influenced by significant regional emissions
191 over the last 12 days, ie. those that are well-mixed and are representative of the mid-
192 latitude of the Northern Hemisphere. A 3-hour period is classed as 'baseline' if recent
193 emissions from Europe or local to Mace Head would not significantly contribute or if
194 there is significant influence from southerly latitudes. The 'local' criterion is designed
195 to exclude low wind and stable boundary layer situations when local topographic or
196 heating effects can result in complex wind features, e.g. land or sea breezes, which are
197 not resolved by the underpinning NAME meteorology and when an emission local to
198 Mace Head would have a significant influence on observations. Southerly air masses
199 are excluded because of the impact of potentially strong hemispheric gradients.
200
201 In this work, two independent sets of meteorology have been used to drive NAME;
202 the UK Met Office's numerical weather prediction model, the Unified Model
203 (referred to as UKMO) and the recently available ECMWF (European Centre for
204 Medium Range Weather Forecasts) re-analysis meteorology, European Centre
205 ReAnalysis-Interim (referred to as ERAI). ERAI meteorology is used from January
206 1996 until December 2002. UKMO is used from January 2003 onwards. The
207 meteorology was changed because ERAI was only available until the end of 2008 and
208 UKMO, pre-2003, was of a lower vertical resolution. The period of overlap is large

and when the baselines estimated using the different meteorologies are compared, the differences are negligible. This is because the choice of meteorological fields only influenced whether the instrumental data were selected as baseline or not. Because the instrumental levels showed little variability during these unpolluted conditions, the precise details of the trajectory path taken were relatively unimportant. The meteorology from both models is defined as analysis i.e. they are short-term forecasts (0-3 hours) that are systematically corrected by the available meteorological observations, both satellite and surface. UKMO has a horizontal resolution of ~60 km pre-December 2005 and then ~40 km onwards, the number of vertical levels used by NAME, and within UKMO has increased over the study period reflecting improved computing capacity ERAI has a horizontal resolution of 0.75^{o} (~80 km) and the lowest 37 vertical levels are used.

Figure 1 shows a composite of all air mass history maps assigned to the baseline category for 1998. The colours of the pixels in the plot in Figure 1 show the contribution to the air concentration at Mace Head from emissions at that point, with deeper colours showing larger contributions. In this way, we can be sure that the transport was intercontinental in scale for all periods allocated to the baseline category and not significantly influenced by transport from Europe or from the tropics.

3. TGM levels in baseline air masses

The origins of the air masses arriving at the atmospheric baseline station at Mace Head, Ireland during each hour of the period from September 1995 to December 2009 inclusive were determined using the NAME model as described above. Those air

masses assigned to the baseline category on a three-hourly basis were extracted from the complete dataset to form a baseline meteorological dataset. The hourly average TGM observations during defined baseline periods were extracted and used to form a baseline TGM dataset. Over the 14 year period of this study, a total of 40404 TGM observations were assigned to baseline air masses, representing a data capture of 32.9%, somewhat lower than the maximum possible of about 50% because of the limited data capture of the TGM instrument over the extended period. Calendar month averages for baseline TGM were then estimated and these monthly averages are tabulated in Table 1. No lower limit value was set on the number of hourly observations needed to characterise a valid monthly average. Figure 2 shows the monthly mean baseline values as a time series.

The seasonal cycle obtained by averaging all the January, then February and so on, monthly mean TGM levels over the period from January 1996 to December 2009 is shown in Figure 3. These average monthly baseline means show evidence of a seasonal cycle with somewhat higher levels during the period from November to April and somewhat lower levels during May to October which is in good agreement with previous observations at this site (Ebinghaus et al., 2002) and other studies. This has been explained by the oxidation potential of the atmosphere (Slemr, 1996; Brosset, 1982). Baseline TGM levels at Mace Head are highest in March and lowest in September. Such seasonal cycles appear to be consistent with those observed at Mace Head, Ireland for a wide variety of trace gases. It is suggested that beside seasonally variable oxidation potential, meteorological variability is the most important factor in the establishment of the observed seasonal cycle of the TGM

concentrations. Temporal dynamics of TGM are complex, with the magnitude of diurnal and seasonal changes often being larger than annual changes.

The presence of trends was investigated with the application of the Mann-Kendall test and Sen's slope estimate (Salmi et al., 2002) to the monthly baseline levels in Table 1. The results of the trend analysis are summarised in Figure 4. Annual baseline TGM means decreased from about 1.8 ng m^{-3} at the start of the record in September 1995 to about 1.4 ng m^{-3} in 2009 as shown in Figure 2. They showed a highly statistically significant negative (downwards) trend of -0.028 ± 0.01 ng m^{-3} yr^{-1} (at the 99.9% level of significance). October and November monthly baseline means also showed highly significant negative (downwards) trends of -0.033 ± 0.1 ng m^{-3} yr^{-1} and -0.048 ± 0.02 ng m^{-3} yr^{-1}, respectively (at the 99.9% level of significance). Those for March and December were also significantly downwards at the 99% level of significance and for January, April, June, August and September at the 95% level of significance. In contrast, the means for February and May showed no statistically significant trends and those for July showed a weak but statistically significant negative (downwards) trend of -0.008 ± 0.006 ng m^{-3} yr^{-1} (at the 95% level of significance). There is therefore some evidence of a decrease in the amplitude of the seasonal cycle as a result of the different observed downwards trends between winter and summer.

4. Discussion and conclusions

In this study, we have characterised the concentrations of TGM in baseline air masses arriving at Mace Head, Ireland after having traversed the North Atlantic Ocean. Over a 14-year period, a statistically significant negative (downwards) trend of -0.028 ±

283 0.01 ng m^{-3} yr^{-1}, representing a trend of 1.6 – 2.0% per year, has been detected in the
284 TGM levels in these baseline air masses. Here, we set our results in the context of the
285 available literature studies of atmospheric Hg trends.
286
287 Slemr et al. (2003) attempted to reconstruct the worldwide trend of atmospheric Hg
288 (TGM) concentrations from long-term measurements of known documented quality at
289 6 sites in the Northern Hemisphere, 2 sites in the Southern Hemisphere, and multiple
290 ship cruises over the Atlantic Ocean made since 1977 and up to 2002. The authors
291 interpreted this information to suggest that the TGM concentrations in the global
292 atmosphere had been increasing since the first measurements in 1977 to a maximum
293 in the late 1980s, after which Hg concentrations decreased to a minimum in 1996 and
294 then remained constant at a level of about 1.7 ng m^{-3} in the Northern Hemisphere. It
295 was also hypothesized that the observed temporal profile was primarily the result of
296 the trends in global Hg use, supply, and emissions.
297
298 In contrast, Lindberg et al. (2007) have pointed out a number of reasons to support the
299 null hypothesis, that there has been little change in TGM since 1977. Additional
300 support for this hypothesis was provided by TGM measurements for the Southern
301 Hemisphere. TGM results for the Southern Hemisphere do not suggest that there has
302 been much change in TGM levels in the remote atmosphere over the past 25–30 years
303 (Sprovieri and Pirrone, 2000; Sprovieri et al., 2002). Although it may appear that
304 these competing hypotheses concerning atmospheric TGM levels in recent times are
305 in conflict, such conflict often aids the development of research strategies. It points to
306 the importance of long-term atmospheric Hg monitoring and the need for additional
307 sites, especially in the remote Southern Hemisphere.

In contrast, recent estimates indicate that Asian emissions are of global importance and are rapidly increasing, at least during the past decade (Streets and Zhang, 2009; Pacyna et al., 2010). Furthermore, experimental data are showing long-range transport across the Pacific and suggest a significant underestimate of Asian mercury emissions (Jaffe et al., 2005).

However, potentially increased Asian emissions are not reflected in the Mace Head baseline TGM data and the negative (downwards) trends reported in this study. The observed decrease from 1.8 ng m^{-3} to 1.4 ng m^{-3} corresponds to a decline of about 25 % over the 14 years period of measurements. This decline is large in comparison to that seen in other trace gases and contradicts the constant or increasing mercury emissions reported in global emission inventories (Streets and Zhang, 2009; Pacyna et al., 2010; Pirrone et al., 2009).

The reason for this apparent conflict between the Mace Head observations of decreasing baseline TGM levels and the global mercury emission inventories that point to increasing mercury emissions is not yet clear. It may be resolved if it is assumed that there is an increasing trend in the rate of atmospheric mercury removal. There is some evidence that tropospheric ozone levels have been increasing during the 20^{th} century and that they have more than doubled since pre-industrial times (Volz and Kley, 1988). If ozone is indeed the chief oxidant for mercury, then an increase in the rate of atmospheric mercury cycling is a distinct possibility. However, there has been some suggestion that the mercury-ozone reaction may not be the chief removal process for elemental mercury (Calvert and Lindberg, 2005) and that atmospheric

bromine processes may be more important (Holmes et al., 2009). If this is the case, then an increase in mercury cycling would be more difficult to justify.

Another hypothesis presented by Slemr et al., (2010) postulates that there has been a substantial shift in the biogeochemical cycle of mercury through the atmosphere, oceans and soil reservoirs. Slemr et al., 2010 suggest decreasing reemissions from the legacy of historical mercury emissions as an explanation for the decline of the global atmospheric mercury pool despite constant or increasing anthropogenic emissions. Decreasing re-emissions of mercury would be entirely consistent with our observations of significant negative (downwards) trends in baseline TGM levels at Mace Head, Ireland.

Acknowledgements

RGD, AJM and the operation of the Mace Head station was supported by the Climate and Energy: Science and Analysis Division of the Department for Energy and Climate Change UK, under contracts EPG 1/1/130 and 142, CPEG 11, 24 and 27, GA 01081, GA 0201 and CESA 002.

The Irish Environmental Protection Agency, through its Climate Change Research Programme is acknowledged for the support of the mercury measurement programme at Mace Head

References

Biester, H., et al., 2002. Elevated mercury concentrations in peat bogs of South Patagonia, Chile - An anthropogenic signal, Earth and Planetary Science Letters, 201, 609-620.

Bindler, R., et al., 2001. Mercury accumulation rates and spatial patterns in lake sediments from West Greenland: A coast to ice margin transect. Environmental Science & Technology *35*, (9), 1736-1741.

Brosset, C., 1982. Total airborne mercury and its possible origin. Water Air Soil Pollution 17, 37-50.

Brunke, E.-G., Labuschagne, C., Ebinghaus, R., Kock, H.H., Slemr, F., 2009. Total gaseous mercury depletion events observed at Cape Point during 2007-2008. Atmospheric Chemistry and Physics 10, 1121-1131.

Calvert, J.G., Lindberg, S.E., 2005. Mechanisms of mercury removal by O_3 and OH in the atmosphere. Atmospheric Environment 39, 3355-3367.

Cunnold, D.M., Prinn, R.G., Rasmussen, R.A., Simmonds, P.G., Alyea, F.N., Cardelino, C.A., Crawford, A.J., Fraser, P.J., Rosen, R.D., 1986. Atmospheric Lifetime and annual release estimates for $CFCl_3$ and CF_2Cl_2 from five years of ALE data. Journal of Geophysical Research, 91, 10797-10817.

Dumarey , R., et al., 1985. The accuracy of the vapor-injection calibration method for the determination of mercury by amalgamation/cold vapour atomic absorption spectrometry. Analytica Chimica Acta 170, 337 - 340.

Ebinghaus, R., Kock, H.H., Jennings, S.G., McCartin, P., Orren, M.J., 1995. Measurements of Atmospheric Mercury Concentrations in Northwestern and Central Europe --- Comparison of Experimental Data and Model Results. Atmospheric Environment 29, 3333 - 3344.

Ebinghaus, R., Jennings, S.G., Schroeder, W.H., Berg, T., Donaghy, T., Guentzel, J., Kenny, C., Kock, H.H., Kvietkus, K., Landing, W., Muhleck, T., Munthe, J., Prestbo, E.M., Schneeberger, D., Slemr, F., Sommar, J., Urba, A., Wallschlager, D., Xiao, Z.,

382 1999. International field intercomparison measurements of atmospheric mercury
383 species at Mace Head, Ireland. Atmospheric Environment 33 , 3063-3073.

384 Ebinghaus, R., Kock, H.H., Coggins, A.M., Spain, T.G., Jennings, S.G., Temme, Ch.,
385 2002. Long-term measurements of atmospheric mercury at Mace Head, Irish west
386 coast, between 1995 and 2001. Atmospheric Environment 36, 5267-5276.

387 Faïn, X., et al., 2009. Polar firn air reveals large-scale impact of anthropogenic
388 mercury emissions during the 1970s. Proceedings of the National Academy of
389 Sciences of the U.S.A., 106, 16114-16119, doi:10.1073/pnas.0905117106.

390 Ferrara, R., et al., 2000. Volcanoes as Emission Sources of Atmospheric Mercury in
391 the Mediterranean basin. The Science of the Total Environment, 259, 115-121,
392 doi:10.1016/S0048-0607(00)00558-1.

393 Fitzgerald, W. F., 1995. Is mercury increasing in the atmosphere? The need for an
394 atmospheric mercury network (AMNET). Water, Air, and Soil Pollution 80, 245-254.

395 Fitzgerald, W.F.,Gill, G.A., 1979. Subnanogram determination of mercury by two-
396 stage gold amalgamation and gas-phase detection applied to atmospheric analysis.
397 Analytical Chemistry 51, 1714-1720.

398 Holmes, C.D., Jacob, D.J., Mason, R.P., Jaffe, D.A., 2009. Sources and deposition of
399 reactive gaseous mercury in the marine atmosphere. Atmospheric Environment 43,
400 2278-2285.

401 Jennings, S.G., McGovern, F.M., Cooke, W.F., 1993. Carbon mass concentration
402 measurements at Mace Head, on the west coast of Ireland. Atmospheric Environment
403 27A, 1229-1239.

404 Kim, K.-H., et al., 2005. Atmospheric mercury concentrations from several
405 observatory sites in the Northern Hemisphere. Journal of Atmospheric Chemistry 50,
406 1-24.

407 Lindberg, S. E., et al., 2007. A Synthesis of Progress and Uncertainties in Attributing
408 the Sources of Mercury in Deposition. Ambio, 36, 19-32.

409 Manning, A.J., Ryall, D.B., Derwent, R.G., Simmonds, P.G., O'Doherty, S., 2003.
410 Estimating European emissions of ozone-depleting and greenhouse gases using
411 observations and a modeling back-attribution technique. Journal of Geophysical
412 Research 108, D4405, doi:10.1029/2002JD002312.

413 Manning, A.J., O'Doherty, S., Jones, A.R., Simmonds, P.G. and Derwent, R.G.
414 Estimating UK methane and nitrous oxide emissions from 1990 to 2007 using an
415 inversion modelling approach. In press Journal of Geophysical Research,
416 doi:10.10.29/2010JD014763.

417 Mason, R. P., 2009. Mercury emissions from natural processes and their importance
418 in the global mercury cycle, in Mercury Fate and Transport in the Global Atmosphere,
419 edited by N. Pirrone and R. P. Mason, Springer, Dordrecht.

420 Munthe, J., Wängberg, I., Iverfeldt, Å., Lindqvist, O., Strömbereg, D., Sommar, J.,
421 Gårdfeldt, K., Petersen, G., Ebinhaus, R., Prestbo, E., Larjava, K., Siemens, V. 2003:
422 Distribution of atmospheric mercury species in Northern Europe: final results from
423 the MOE project, Atmospheric Environment, 1, 9-20.

424 Oltmans, S.J., Levy, H. II, 1994. Surface ozone measurements from a global network,
425 Atmospheric Environment 28, 9-24

426 Pacyna, E., Pacyna, J.M., Steenhuisen, F., Wilson, S., 2006. Global anthropogenic
427 mercury emission inventory for 2000. Atmospheric Environment 40, 4048-4063.

Pacyna, E. G., Pacyna, J.M., Sundseth, K., Munthe, J., Kindborn, K., Wilson, S., Steenhuisen, F., Maxson, P., 2010. Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. Atmospheric Environment 44, 2487-2499.

Pirrone, N., Allegrini, I., Keeler, G.J., Nriagu, J.O., Rossmann, R., Robbins, J.A., 1998. Historical atmospheric mercury emissions and depositions in North America compared to mercury accumulations in sedimentary records. Atmospheric Environment 32, 929-940.

Pirrone, N., Keeler, G.J., Nriagu, J.O., 1996. Regional Differences in Worldwide Emissions of Mercury to the Atmosphere. Atmospheric Environment 30, 2981-2987.

Pirrone, N., et al., 2009. Global mercury emissions to the atmosphere from natural and anthropogenic sources, in Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements, and Models, edited by N. Pirrone and R. P. Mason, pp. 3-49, Springer.

Ryall, D.B., Maryon, R. H., 1998. Validation of the UK Met Office's NAME model against the ETEX dataset. Atmospheric Environment 32, 4265-4276.

Ryall, D.B., Maryon, R.H., Derwent, R. G., Simmonds, P.G., 1998. Modelling long-range transport of CFCs to Mace Head, Ireland. Quarterly Journal of the Royal Meteorological Society 124, 417-446.

Salmi, T., Maata, A., Antilla, P., Ruoho-Airola, T., Amnell, T. 2002. Detecting trends of annual values of atmospheric pollutants by the Mann-Kendall test and Sen’s slope estimates – The Excel template application Makesens. Finnish Meteorological Institute, Helsinki, Finland.

451 Schroeder, W.H., et al., 1995. International field intercomparison of atmospheric
452 mercury measurement methods. Water Air and Soil Pollution 80, 611-620.

453 Simmonds, P.G., Cunnold, D.M., Dollard, G.J., Davies, T.J., McCulloch, A., Derwent,
454 R.G., 1993. Evidence for the phase-out of CFC use in Europe over the period 1987-
455 1990. Atmospheric Environment 27A 1397-1407.

456 Simmonds, P.G., Seuring, S., Nickless, G., Derwent, R.G., 1997. Segregation and
457 interpretation of ozone and carbon monoxide measurements by air mass origin at the
458 TOR station Mace Head, Ireland from 1987 to 1995. Journal of Atmospheric Chemistry
459 28, 45-49.

460 Slemr, F., Brunke, E., Ebinghaus, R., Temme, C., Munthe, J., Wangberg, I.,
461 Schroeder, W., Steffen, A., Berg, T., 2003. Worldwide trend of atmospheric mercury
462 since 1977. Geophysical Research Letters 30, 1516, doi:10.1029/2003GL016954.

463 Slemr, F., 1996. Trends in atmospheric mercury concentrations over the Atlantic
464 Ocean and the Wank summit and the resulting constraints on the budget of
465 atmospheric mercury, in: Baeyens, W., Ebinghaus, R., Vasiliev, O. (eds) Global and
466 Regional Mercury Cycles: Sources, fluxes and mass balances, NATO ASI Series 2.
467 Environment Vol. 21, Kluwer, Dordrecht, The Netherlands, pp 33-84.

468 Sprovieri, F., Pirrone, N., 2000. A preliminary assessment of mercury levels in the
469 Antarctic and Arctic troposphere. Journal of Aerosol Science 31, 2-.

470 Sprovieri, F., Pirrone, N., Hedgecock, I.M., Landis, M.S., Stevens, R.K., 2002.
471 Intensive atmospheric mercury measurements at Terra Nova Bay in Antarctica during
472 November and December 2000. Journal of Geophysical Research 107,
473 4722,doi:10.1029/2002JD002057.

474 Streets, D. G., Zhang, Q., 2009. Projections of global mercury emissions in 2050,
475 Environmental Science and Technology 43, 2983-2988.

476 Urba, A., Kvietkus, K.; Sakalys, J.; Xiao, Z.; Lindqvist, O., 1995. A new sensitive and
477 portable mercury vapor analyzer Gardis-1A. Water Air and Soil Pollution 80, 1305-
478 1309.

479 Volz, A., Kley, D., 1988. Evaluation of the Montsouris series of ozone measurements
480 made in the nineteenth century. Nature 332, 240-242.
481

Table 1. Monthly average concentrations of total gaseous mercury in ng m^{-3} baseline air masses arriving at Mace Head, Ireland over the period from February 1996 to December 2009.

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1996		1.55	2.60	2.06	1.59	1.88	1.94	1.71	1.66	1.62	2.20	1.80
1997	1.76	1.90	1.70	1.85	1.55	1.55	1.54					
1998					1.63	1.68	1.59	1.66	1.51	1.93	1.98	2.00
1999	2.00	1.79	1.92	1.68	1.56	1.69	1.58	1.45	1.51	1.69	1.96	2.12
2000	1.95	1.90	1.97	2.11	1.91	1.74	1.63	1.69	1.57	1.67	1.68	1.67
2001	1.60	1.57	1.73	1.92	1.61	1.54	1.62	1.52	1.54	1.66	1.63	1.56
2002	1.87	1.87	1.80	1.90	1.82	1.67	1.42	1.46	1.75	1.59	1.75	1.87
2003	1.65	1.65	1.73	1.53	1.52	1.59	1.63	1.68	1.50	1.57	1.75	1.82
2004	1.63	1.79	1.77	1.55	1.60	1.63	1.60	1.43	1.56	1.53	1.59	1.64
2005					1.55	1.66	1.61	1.59	1.49	1.47	1.53	1.53
2006	1.55	1.62	1.59	1.57	1.44	1.38	1.41	1.31	1.25	1.46	1.58	1.55
2007	1.61	1.56	1.60	1.75	1.74	1.59	1.52	1.48	1.56	1.47	1.58	1.59
2008	1.77	1.68	1.62	1.57	1.56	1.55	1.59	1.46	1.39	1.50	1.56	1.44
2009	1.43	1.53	1.51	1.53	1.37	1.35	1.39	1.38	1.33	1.29	1.40	1.45

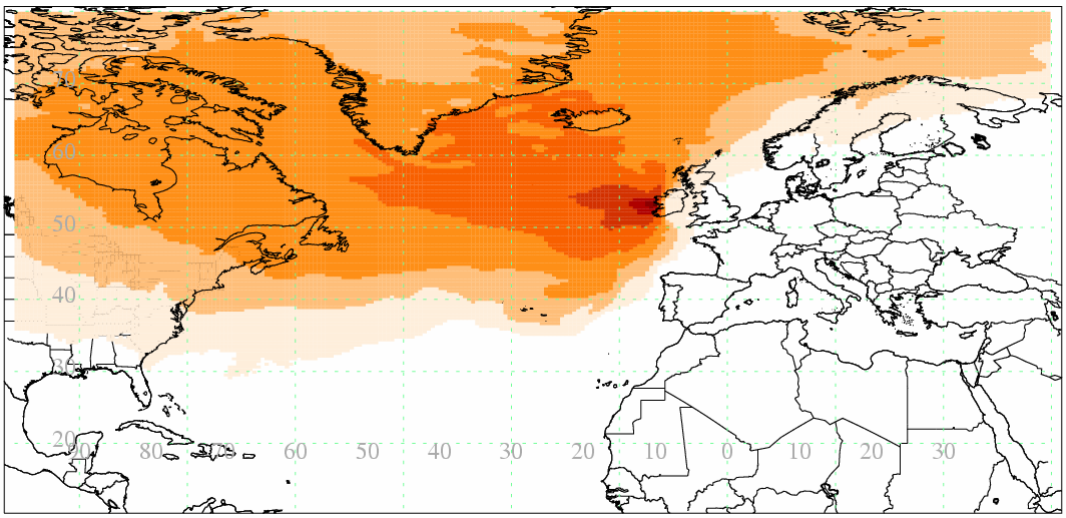
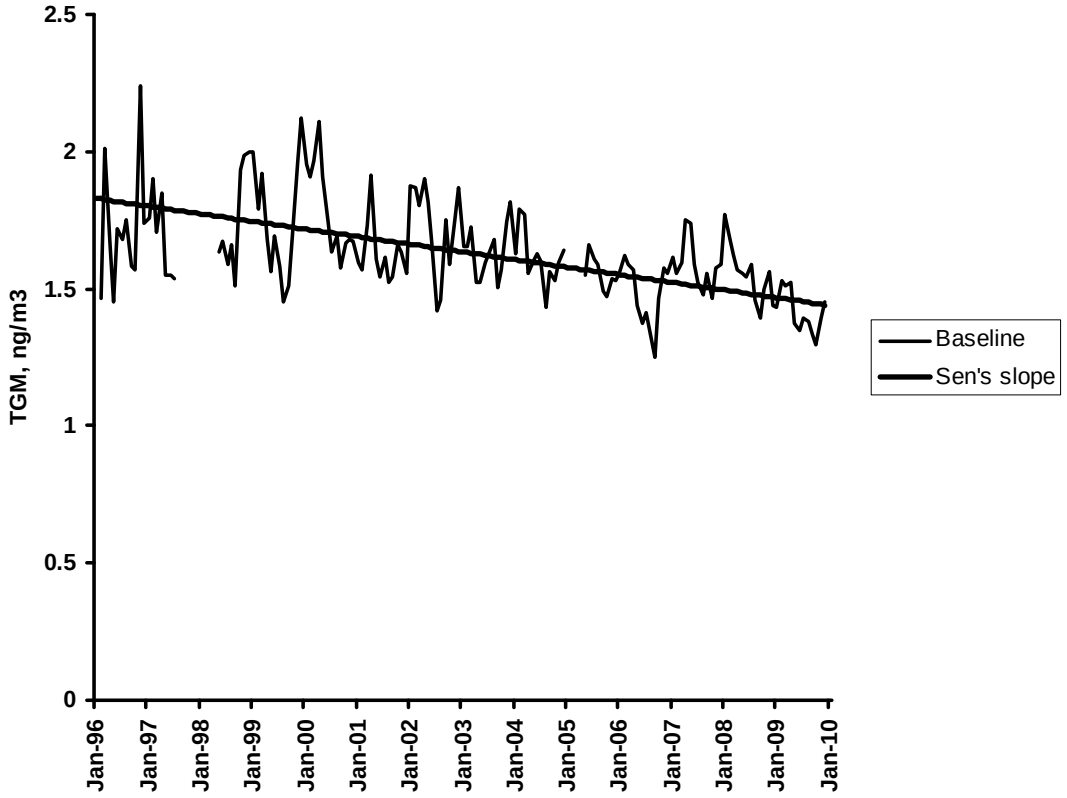


Figure 1. A composite of the back attribution plots for Mace Head, Ireland for all air masses assigned to the baseline category during 1998, with the pixel colours showing the relative contribution to the air concentration at Mace Head, Ireland from the emissions of an inert tracer at that location.



496
497
498 Figure 2. Time series of monthly mean baseline TGM levels at Mace Head, Ireland
499 over the period from 1996 to 2009, also showing the fitted trend based on the Mann-
500 Kendall test and Sen's slope.

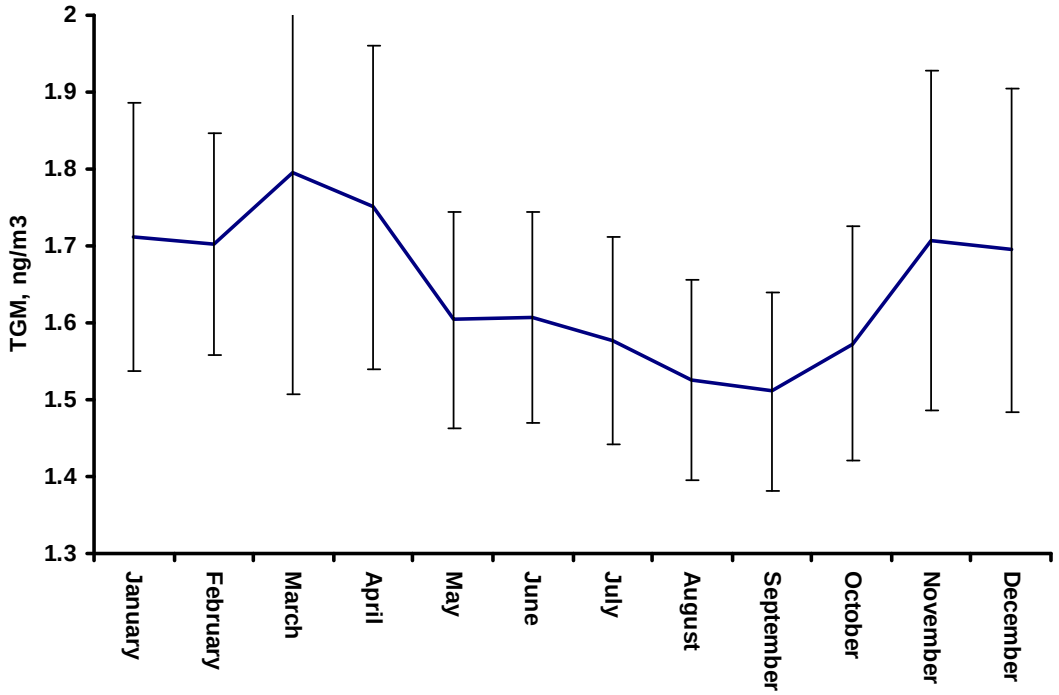


Figure 3. Average monthly mean TGM levels in baseline air masses arriving at Mace Head, Ireland between February 1996 and December 2009.

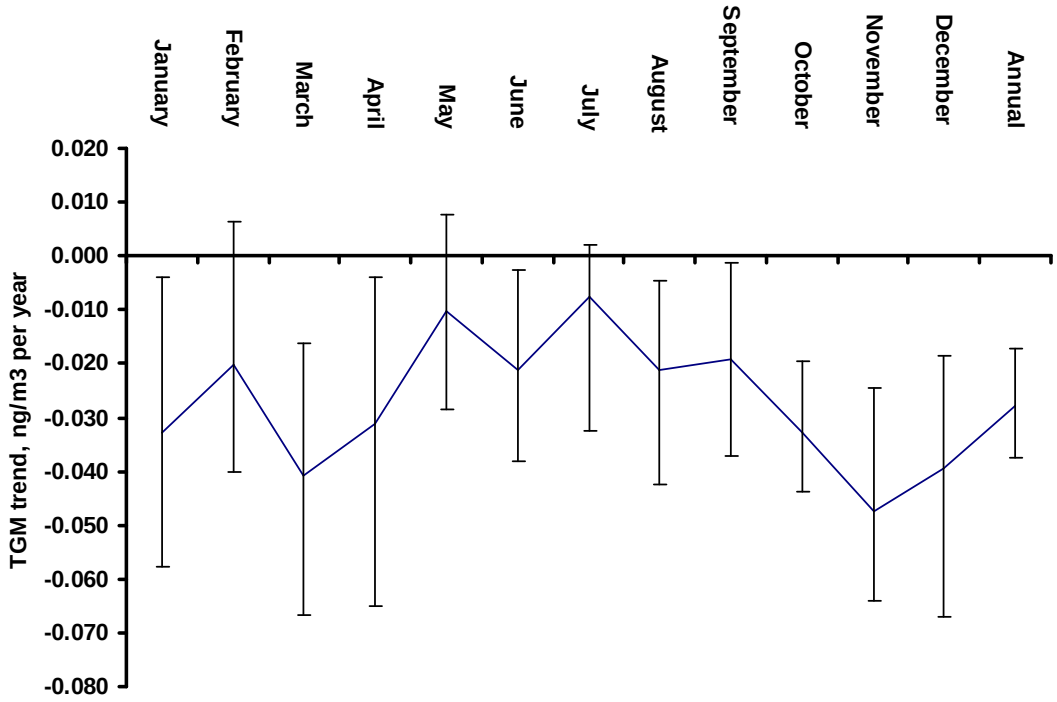


Figure 4. Trends in the monthly mean baseline TGM levels together with the 95% confidence limits over the period from February 1996 to December 2009 determined with the application of the Mann-Kendall test and Sen's slope estimate (Salmi et al., 2002).