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Development of a method for the sampling and determination of particulate mercury in the atmosphere

Degree of candidata scentiarium

Siri Sekkesæter

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THESIS FOR THE DEGREE OF CANDIDATA SCIENTIARUM

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Preface

This thesis was performed at the University of Science and Technology (NTNU) in Trondheim in addition to the Norwegian Institute for Air Research (NILU) at Kjeller during the period between September 1999 and September 2001. The experimental section of this work was carried out at NILU during year 2000.

Dr. Eiliv Steinnes at the Department of Chemistry, NTNU, has been chief supervisor while Dr. Torunn Berg at NILU has been associate (external) supervisor.

The thesis is organized in nine chapters. Chapter 5: *Experiences made along the way,* is not necessary to obtain a complete understanding of this work. Still it is included as means of enlightening future developers of the method dealt with here. This chapter will present some tests and efforts, which eventually were considered as dead ends. Hopefully this information will save researchers to come for unnecessary work and time.

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I also wish to thank Dr. Julia Lu at Environment Canada for sharing her experience on the method treated in this work.

My fellow student Anne-Kari Valdal, with whom I have shared office and fieldwork experiences, I wish to thank for fruitful discussions and devoted moral support.

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Trondheim/Kjeller, September 2001

Siri Sekkesæter

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Summary

Total particulate mercury constitutes a small percentage of the total mercury present in the atmosphere. Despite the low concentration, normally in the order of 1 – 50 pg m^{-3}, the particulate phase plays an important role for determining the deposition fluxes of mercury.

The goal has been to implement the use of a custom-made quartz trap for measuring total particulate mercury (TPM) in the atmosphere. This new method, developed by Canadian scientists, is an improvement compared to conventional methods, as a minimum of sample handling steps is required between sampling and analysis. Two miniature quartz tubes are put together by a piece of silicon tubing. The conjunction of the tubes holds a filter disk, 10 mm in diameter, cut out from a quartz fiber filter. The filter disk is supported by a nickel screen support. Prior to sampling the TPM-trap is cleaned by heating it to 900 °C until a constant background signal is observed. During sampling air is pulled through the trap at a flow rate of approximately 5 l min^{-1}. Particles bigger than 0.3 μm in diameter are collected on the filter. A custom-made sampling box was developed to make outdoor sampling feasible.

An analytical system was constructed/adapted to obtain direct insertion of the TPM-trap into an analytical train. A custom-built oven, which heats the sample to 900 °C for 3.5 - 10 minutes was developed. At this temperature all mercury species present are reduced to Hg° and transported by carrier gas (O_2, Ar) to an atomic fluorescence spectrometer for detection. The achievement of a satisfactory analytical system was problematic due to high background levels and unstable results of standard injections.

During May 2000 a fieldwork was carried out at Ny-Ålesund, Spitsbergen. The occurrence of gaseous mercury depletion episodes coupled with elevated levels of more reactive mercury species such as TPM and GDM makes the period following polar sunrise of special interest. Field measurements were also performed at different positions on the Mediterranean Sea during a fortnight at the beginning of August 2000.

A functioning analytical system was finally achieved during September 2000. Accuracy and precision were evaluated and found to be satisfactory. Field samples were analysed. The Ny-Ålesund samples were higher than the expected range. This was probably due to some sort of contamination since the field blank values were even higher than the actual samples. The results of the samples made on the Mediterranean Sea were in the lower section of the expected range of 10-50 pg m^{-3}. Parallel sampling of three and four TPM-traps was performed outside the NILU quarters at Kjeller. The results were in the range between 6 and 99 pg m^{-3}, but generally the precision of the parallels was poor.

Extensive testing with standard reference material supplied on numerous traps revealed an error as individual traps produced a certain recovery concentration of the true value. It is reasonable to assume that this systematic error apply also when TPM-traps are used for sampling. Hence, reliable sampling and determination of particulate mercury in ambient air by usage of TPM-traps cannot be performed at the present stage. The results obtained in the different field studies by the TPM-trap method must be seen in the light of this assumption.

During the fieldworks at Ny-Ålesund and Kjeller, TPM was also sampled on glass fiber filters (142 mm) installed in stationary high volume samplers. These filters were digested in acid and analysed by using a vapour generator coupled to the atomic fluorescence detector. The

accuracy and precision of this procedure was judged to be satisfactory. Some tests were performed in order to optimise the acid digestion procedure of this method.

Development of a method for the sampling and determination of particulate mercury in the atmosphere

1 Introduction

Mercury is present in the atmosphere predominantly in the gaseous elemental state (Hg°), which is volatile and relatively unreactive. However, a small percentage of more reactive mercury species are also present. The most significant are mercury associated with particles (Hg_{part}) and divalent gaseous mercury (GDM). In recent years, increased attention has been devoted to these more reactive forms, as they are believed to play an important role in the cycle of mercury between the different compartments of nature. Although Hg_{part} and GDM only constitute 1-5% of the total mercury in the atmosphere, they have chemical and physical properties which make them likely to govern a substantial part of the total deposition of mercury.

In order to map the cycling of mercury between the atmosphere and the ground, it is imperative to have reliable methods for sampling and analysis of the different species of mercury. The extremely low concentrations of Hg_{part} and GDM in ambient air, in the order of picograms per cubic meter of air, make this task a challenge. Different methods have been applied and are continually in development. GDM is generally sampled on denuders coated with KCl, but other methods are also in use. For particulate mercury, sampling on different kinds of filters, or on quartz wool, has been tested. However, a new method developed by Julia Lu (Environment Canada), was introduced in the mid-nineties: a miniature custom-made quartz trap (TPM-trap) is used for sampling Hg_{part}. It is an improvement compared to conventional methods as the number of sample handling steps required is reduced to a minimum.

Gaseous elemental mercury (Hg°) present in the atmosphere at a concentration of a few nanograms per cubic meter air is sampled by amalgamation on gold traps. Advanced monitors, which are able to automatically sample and determine Hg° with five minutes resolution, have been available on the market for some years now. The introduction of these high-resolution mercury monitors at Arctic research locations has revealed a most interesting phenomenon. During the period following polar sunrise, frequent episodes have occurred where the concentration of Hg° decreases from ~1.5 ng m^{-3} to less than 0.2 ng m^{-3} (Schroeder et al., 1998). A few measurements of particulate mercury indicate that this species is increasing substantially at the same time (Lu et al., 1998). It is likely that the specific chemical and physical conditions that occur in the Arctic during spring lead to incidents of transformation of Hg° to Hg_{part} and GDM. Compared to vapour phase mercury, both particulate mercury and GDM have got shorter residence times and higher deposition rates. Thus, this transformation introduces elevated levels of mercury to the sensitive terrestrial and aquatic ecosystems at a time of year when biota is preparing for peak summer activity.

The overwhelming majority of mercury in air is Hg°, but the much larger wet scavenging and/or dry deposition rates for divalent and particulate mercury can have a significant impact on mercury deposition rates, especially near sources of these compounds. Important emission sources are burning of fossil fuels, waste incineration plants and crematoriums, but also natural sources such as volcanoes and erosion of certain rocks contribute. The areas surrounding the Mediterranean Sea experience elevated concentrations of atmospheric mercury compared to the rest of the European continent. This is due to both anthropogenic and natural sources.

Once introduced into the atmosphere Hg° can circulate for a long period of time (Berg et al., 2001). It can be deposited and re-emitted in several steps between the atmosphere and terrestrial and aquatic ecosystems. There is a general agreement in the scientific community that the marine ecosystem can be both a sink for and a source of mercury, which is cycling through the global environment. Thus, it is necessary to measure these fluctuations of mercury in order to estimate a global budget for this toxic element.

During the summer of 2000, a research project was initiated to investigate the air-sea exchange of different mercury species over the Mediterranean Sea.

The aim of this study was to implement the use of a modified version of the Canadian TPM-trap in the laboratory at the Norwegian Institute for Air Research (NILU), Kjeller, Norway. Both a system for sampling and for analysis of total particulate mercury was constructed. Further on, the intention was to carry out measurements in relevant environments.

A field study was carried out in the Norwegian Arctic in May 2000. Particulate mercury was measured with two methods: 1: TPM-trap and 2: glass fiber filters installed in stationary high volume samplers. The main objective was to support the existing theory of transformation reactions of Hg° to the more reactive species (TPM and GDM) in the Arctic during the period following polar sunrise.

Field measurements with the TPM-trap were carried out at different locations on the Mediterranean Sea in July-August 2000 as participation of a preliminary study of the air-sea exchange of atmospheric mercury. Parallel sampling of TPM performed by the undersigned and an Italian research group (CNR-Institute for Atmospheric Pollution) also using TPM-traps, opened for comparison of results.

This thesis presents results of method development and evaluation in addition to particulate mercury data from the above-mentioned field studies as well as TPM data from field measurements of Hg_{part} performed outside the NILU quarters at Kjeller, autumn 2000.

2 Background

2.1 Mercury – an introduction

Mercury is considered a global pollutant because of its potential for long-range transport via the atmospheric pathway and deposition in ecosystems remote from anthropogenic Hg sources (Gustin et al., 2000).

2.1.1 History

Among the vast number of chemicals known to mankind, mercury is one of the most unique, due to its long history, toxicity, chemical, and physical properties. This element was known to the ancient Chinese and Hindus, and has been found in Egyptian tombs from 1500 B.C. The Phoenicians traded cinnabar (HgS, used as the pigment vermilion) from around 700 B.C. Mercury's ability to separate precious metals such as gold and silver from their ores by amalgamation was known as early as 500 B.C. and is still used today for gold extraction in the Amazon region (Olmez and Ames, 1997).

2.1.2 Properties

Mercury has the chemical symbol Hg, which originates from the Latin name hydrargyrum meaning watery silver. It is the only metal that is liquid at room temperature and is found among the transition elements in the Periodic Table in Group IIB along with zinc and cadmium. As can be seen from the oxidation potentials ($E°$ for $M = M^{2+} + 2e^-$ is 0.762, 0.402 and –0.854 V for Zn, Cd and Hg respectively), zinc and cadmium are fairly electro positive, whereas mercury is relatively inert. Elemental mercury ($Hg°$) readily combines with noble metals (Au, Ag, Pt, Pd) to form alloys (amalgams). Other unique and/or technologically important physico-chemical properties include: high surface tension ($Hg°$ does not wet glass), high specific gravity, low electrical resistance, and a constant volume of expansion over the entire temperature range of its liquid state. Some physical properties of mercury are listed in Table 1.

Table 1: Physical data for elemental mercury

Symbol	Hg
Atomic number	80
Atomic weight	200.59
Melting point	-39 °C
Boiling point	357 °C
Density	13.69 g cm^{-3}
Oxidation states	0, +1, +2
Henry's law constant at 20 °C	729 Pa m^3 mol^{-1}
Vapour pressure at 20 °C	0.180 Pa
$E°$ ($Hg = Hg^{2+} + 2e^-$)	-0.845 V

Source: Schroeder and Munthe (1998).

2.1.3 Levels in the natural environment

In nature mercury mainly occurs as sulphide (cinnabar), and occasionally as chloride or oxide (Lin and Pehkonen, 1999). The mercury level of typical crust material ranges from a few to several hundred parts per billion, with some common mineral cores as high as a few hundred parts per million. Natural waters, including the oceans and inland fresh waters, contain Hg in the concentration order of 0.5 to 5 nanograms per litre. The mercury in ocean waters is stabilized as $HgCl_4^{2-}$ (Olmez and Ames, 1997). The atmospheric mercury concentration is in the range of 1 to 4 ng m^{-3} (Slemr and Langer, 1992). In rain water the total concentration of mercury is usually in the range from 1-25 ng l^{-1} (with peak values up to 100 ng l^{-1}) (Lindqvist et al., 1991).

2.2 Sources and sinks

Metallic mercury and mercury compounds occur naturally in the environment, but are normally present at low levels. However, certain types of minerals, such as cinnabar (HgS), contain enriched levels of this element. Hg along with other heavy metals is generally present at trace concentrations in ores, coal and oil. Combustion of fossil fuels and production of several minerals consequently emits certain amounts of mercury. Hence Hg has both anthropogenic and natural sources.

Relative contributions of natural and anthropogenic sources to the environment are uncertain and hence is a subject continuously discussed. A study made by Mason and co-workers (1994) concludes that approximately two-thirds of the present mercury fluxes to and from the atmosphere are directly or indirectly of anthropogenic origin. They estimated that anthropogenic and natural sources account for ~4000 tonnes year^{-1} and 2000 tonnes year^{-1} respectively. Pacyna and Pacyna (2000), on the other hand, assume that the natural contribution of mercury is 3000 tonnes per year, constituting 60% of the total global emission of mercury. Once mercury has been released into the natural environment, its original source, whether anthropogenic or natural, can no longer be discerned. Still there seems to be a general consensus on the fact that there has been a vast increase in the mercury levels since preindustrial times due to anthropogenic sources by a factor of 2-10 (depending on the geographical area) (Steinnes and Andersson, 1991). When it comes to recent decades, data from the period 1977-1990 show an increase in the global TGM concentration. Measurements during the period 1990-1994 revealed a significant decrease of ~21%. This however, is difficult to reconcile with current anthropogenic emission inventories, implying a constant human-made contribution predominantly originating from coal combustion and waste incineration (Slemr et al, 1985; Slemr, 1996; Slemr and Scheel, 1998).

2.2.1 Natural sources

Mercury is released or re-emitted into the atmosphere by a number of natural processes/emission sources including outgassing of the earth’s mantle/crustal material, evasion from the surficial soils, water bodies (both fresh and salt water), vegetation surfaces, wild fires, volcanoes, and geothermal sources. Re-emission involves gaseous evasion of previously deposited Hg. Mercury is thought to be released from natural sources mainly as Hg° vapour, but mercury bound to particulate matter/aerosols may originate from some natural sources like volcanoes and soil erosion. Emissions of other species such as dimethyl mercury (DMHg) and volatile inorganic Hg compounds cannot be ruled out, though these species are not stable in the atmosphere (Schroeder and Munthe, 1998).

Estimates of mercury emissions from natural sources, published between 1970 and 1982, was reviewed by Lindqvist and Rodhe (1985). Confronted with values that ranged from 2500 to 30 000 tonnes per year for natural Hg emissions globally, these authors considered the lower end of the given range as the most reliable. Since then, Nriagu and Pacyna (1988) have estimated global natural mercury emissions to be approximately 3000 tonnes per annum. Diffuse naturally mercury-enriched areas represent long-lived sources of mercury. Emissions from such natural sources need to be better constrained in order to assess the effectiveness of regulations and controls for Hg emissions imposed on point sources (Gustin et al., 2000).

The different compartments in nature can be regarded as both sources and sinks of mercury. Mercury released into the atmosphere may deposit in terrestrial and aquatic environments, these now working as sinks. During the summer months with elevated temperatures, the mercury can be re-emitted into the atmosphere. Aquatic and terrestrial surfaces are now working as sources while the atmosphere is the sink (this is further illuminated in chapter 2.5). Ultimately the terrestrial environment and the bottom sediments of the oceans serve as sinks for mercury (Mason et al., 1994).

When considering natural sources of mercury one should bear in mind the fact that the man-made Hg emissions during the last century have been substantial. It is estimated that since 1890 two hundred thousand tonnes of mercury have been emitted to the atmosphere whereas the current atmospheric burden (1994) is only approximately five-six thousand tonnes (Slemr et al., 1985), hence 95-97% of this pool resides in other compartments of nature (EPRI, 1994). Thus a great deal of what may appear to be natural emissions of mercury, especially from the oceans, is actually re-emission of anthropogenically produced mercury (Olmez and Ames, 1997).

The world’s most important deposits of mercury are found in the Mediterranean region. Almaden (Spain), Idrija (Slovenia), Monte Amiata (Italy) are locations where elevated concentrations are found in the crust as cinnabar. Mercury is located in lesser quantities in Peru, California, Mexico, Mainland China, and Japan. The sources around the Mediterranean Sea contribute along with anthropogenic input to increased levels of mercury in this region. The major production of mercury occurs in these areas. As human activities expose the surroundings to significantly higher levels of Hg than in the case where these sources were left untouched, discharges from these areas may be seen as a mixture of anthropogenic and natural sources of mercury.

2.2.2 Anthropogenic sources

During industrial times anthropogenic sources of mercury have been the chlor-alkali production, primary battery production, manufacture of measuring and control instruments, electrical lighting, wiring devices, electrical switches, marine paints, agricultural fungicides, among others. However during the last decades these applications of mercury have declined due to increasing understanding of the toxicity of this element. Today combustion of fossil fuels and incineration of wastes are regarded as major anthropogenic sources. In a study by Pacyna and Pacyna (2000) an estimation of the global emissions of mercury from anthropogenic sources was made. This was based on measurements done in1990 and1995 in more than 150 countries. The following man-made sources were regarded as the current main contributors of mercury:

-combustion of coal
-oil product combustion
-cement production
-lead production
-zinc production
-pig iron and steel production
-caustic soda production
-mercury production
-gold production
-waste disposal, and
-other sources (e.g. crematory incineration)

About 1900 tonnes of mercury were emitted in 1995, which is within the range between 1270 (minimum) and 2140 tonnes (maximum) estimated by Pacyna and Pacyna (1996) for the year 1990. Hence, it can be concluded that no major changes were observed between 1990 and 1995 in estimates of global Hg emissions from anthropogenic sources worldwide. Yet, there was a change with respect to the locations of the major sources. The contributions from Europe and North America had moved below 25% of the total input while Asian countries including China, India, and South and North Korea increased their annual emissions during the period, now being responsible for roughly 56% of the global mercury emission (Pacyna and Pacyna, 2000).

In recent years governments in the western world have implemented great efforts to reduce the anthropogenic discharges of mercury. In Finland, France, Germany and Switzerland among others, there are distillation plants for the extraction of mercury from high concentrated mercury waste, such as amalgam waste and sludge from chlorine-alkali plants.

All the Nordic countries have got disposal facilities for mercury. However, the chemical and physical properties of Hg make it a challenge to store this element without the risk of emission to the surroundings (Nordic Council of Ministers, 1999). Today there is also increasing concern of how to constrain Hg emissions from natural sources (Gustin at al., 2000).

2.3 Speciation

Speciation describes the physicochemical forms of an element that collectively composes its total concentration in a sample. Mercury can exist in a large number of different physical and chemical forms with a wide range of properties. The identification and quantification of individual Hg forms are imperative for addressing questions concerning emission control, toxicity, mobility, bioaccumulation and atmospheric fate and transport because each has distinctive physical, chemical and biological properties. There exist physical and chemical data on over 100 inorganic and organic mercury compounds, however the most important forms of mercury can be divided into three categories; elemental mercury, inorganic ions of mercury and organic mercury compounds (Merian, 1991).

2.3.1 Elemental mercury

Elemental mercury, Hg°, is usually referred to as mercury vapour or gaseous mercury when present in the atmosphere or as metallic mercury in liquid form. It has a relatively high vapour pressure, yielding a concentration in saturated air of 18 mg m^{-3} at 24 °C. In water the solubility is only 49.4 x 10^{-6} g l^{-1} at 20 °C (Schroeder and Munthe, 1998). As vapour mercury exists in a monoatomic state.

2.3.2 *Inorganic ions of mercury*

Mercury exists in the ionic form as Hg^{2+} (mercuric ion) and Hg^{+} (mercurous ion).
Monovalent mercury, commonly present as the dimer Hg_2^{2+}, is rarely stable under environmental conditions (Schroeder and Munthe, 1998). Mercury(I)cloride, Hg_2Cl_2 commonly known as calomel, is probably the most important univalent compound, and is used in calomel electrodes. In contrast to Hg°, divalent mercury is generally reactive and water-soluble. Hg^{2+} acts as a soft acid and forms stable complexes with ligands such as OH^-, Cl^-, Br^-, I^-, S^{2-}, SO_3^{2-} and CN^- (Merian, 1991). In the atmosphere Hg^{2+} is commonly present as $HgCl_2$ (g, l), $Hg(OH)_2$ (g, l), HgO (g, s) and HgS (g, s). It is predominantly divalent mercury compounds which are associated with particles (Seigneur et al., 1998). HgO is the single stable oxide of mercury. At temperatures above 400 °C it will split into Hg° and O_2.

2.3.3 *Organic mercury*

Organic mercury compounds consist of various chemical structures in which mercury forms a covalent bond with carbon. However, most important seen from both an environmental and a toxicological point of view, is the alkyl mercury compounds. The ability of methyl mercury, CH_3Hg^+, to bio-concentrate more than million-fold in the aquatic food chain is the main reason for the concern about emission/mobilization of mercury in the biosphere (Schroeder and Munthe, 1998). In the past, methyl mercury compounds were manufactured as fungicides or appeared as unwanted by-products of the chemical industry. Today the methylation of inorganic mercury by microorganisms in addition to abiological methylation by fulvic acid in aquatic sediments, are the predominant sources of methyl mercury (Clarkson, 1993; Varshal et al., 1996). Both mono methyl mercury (MeHg), CH_3Hg^+, and dimethyl mercury (DMHg), CH_3HgCH_3, are produced. Conditions that enhance bacterial growth also promote methylation processes (Merian, 1991).

2.3.4 *In the atmosphere*

Inventories of both natural and anthropogenic mercury emissions are generally only considering the total amount of mercury released into the atmosphere. Because of their significantly different atmospheric behaviour, at least three species should be explicitly dealt with: Elemental gaseous mercury, Hg° (g), gaseous divalent mercury (GDM), and total particulate mercury (TPM). The differentiation is also important when considering the effectiveness and development of current clean-up technologies (Schroeder and Munthe, 1998).

In addition small quantities of organic Hg-species such as MeHg and DMHg are present in ambient air at pg m^{-3} levels (Brosset and Lord, 1995; Ebinghaus et al., 1994). The sources of the atmospheric methylated forms are not well known. Prestbo and Bloom (1996) suggested degassing of DMHg form the ocean in upwelling areas, followed by chemical degradation to MeHg as one possible source. DMHg is not likely to be extensively recycled owing to its rapid degradation and short residence time in the atmosphere.

2.4 Health effects

Mercury is a toxic element that is non-essential for human beings. Hg is present on the Environmental Authority's (SFT) priority list of chemicals which are to be substantially reduced. Several international binding conventions for reducing mercury discharges have been settled upon, e.g. OSPAR (The Convention for the Protection of the Marine Environment of the North-East Atlantic,1998), The North Sea Declarations and UNECE; Convention on Long-Range Transboundary Air Pollution, among others. There are considerable differences between the various mercury species when it comes to toxicity.

2.4.1 Mercury and medicine

As far back as ancient times mercury was used as a remedy (Aristotle). Arab physicians in the early middle ages made extensive use of mercurial ointments. The ability of mercury compounds to produce salivation also became known at this time and later led to its extensive use in the treatment of syphilis. It was not until 1861 that Overbeck attempted a systematic clinical and experimental study of mercury, which resulted in a clear description of the toxic effects of mercury in man and animals (IAEA, 1972).

2.4.2 Effects on humans

Humans are exposed to mercury by intake of food, in particular fish, as well as via air, drinking water and the release of mercury from dental amalgam. Depending on the type of mercury compound and the mode of contact, the symptoms of intoxication in man vary. Acute mercury poisoning usually results from the accidental or suicidal ingestion of soluble mercury salts, such as mercuric chloride. The effect is severe inflammation of the digestive tract. Abdominal cramps with nausea and vomiting and bloody diarrhoea commonly occur within hours. The absorbed mercury is concentrated in the kidneys, where it damages the blood-filtering structures; as a result, there is first a decrease and then a complete cessation of urine output, causing the accumulation of toxic substances in the blood (uremia), and ultimately, death. Symptoms of chronic mercury poisoning may include a metallic taste and excessive production of saliva; inflammation of the membranes of the mouth; loosening of teeth; the formation of a blue line on the gums; pain, numbness, and tremor in the extremities; loss of weight and appetite; and mental and personality changes marked by depression and a tendency to withdraw (Encyclopaedia Britannica). Methyl mercury and mercuric chloride are listed as possible human carcinogenic substances (Schroeder and Munthe, 1998).

2.4.3 Methyl mercury

Methyl mercury is generally considered to represent the most serious toxicological threat to man and animals (IAEA, 1972). Humans are usually exposed to this species through the intake of contaminated fish. In aquatic food chains MeHg is biomagnified in the order of 10 000 to 100 000 times the concentration in ambient water (Wolfe et al. 1998). Several countries, e.g. Sweden, recommend pregnant and breast-feeding women to desist totally from intake of fresh-water fish such as pike, perch and eel. This corresponds to the fact that the prenatal period is the most sensitive stage of the life cycle to MeHg. This substance can cross the blood-brain barrier, which normally protects the human brain from toxins in the blood stream, and in addition it is able to penetrate the placenta, thus, exposing the foetus to this potent neurotoxin (Schroeder and Munthe, 1998). The severe symptoms following prenatal high dose exposure to MeHg are collectively termed the "Minamata Syndrom", including motor disturbances, seizures, profound retardation and palsy (Harada, 1995). Exposure to lower doses of MeHg via maternal consumption of fish over a prolonged period of time may lead to impairments in neuropsychological functions, particularly those related to language, attention and memory in the offspring (Grandjean et al., 1997). Recent studies have illuminated the negative effects of mercury and methyl mercury on the immune system (Silbergeld and Devine, 2000).

2.4.4 Recommendations in Norway

Administrative norm for maximum Hg concentration in ambient air in a job location is 0.05 mg m^{-3}. For MeHg the value is 0.01 mg m^{-3} (Lovdata, 1996). For drinking water the maximum level of mercury allowed is 0.5 µg l^{-1} (SNT, 1995). According to the Norwegian National Foodstuff Agency, mercury levels in fish and fish products shall not exceed 0.5 mg kg^{-1} (SNT, 1994). Further, pregnant and breast-feeding women are advised not to consume freshwater pike and perch longer than 25 cm and lake trout weighing more than 1 kg. In general adults are recommended a limited consumption of these fish species of once a month on average (SNT).

2.5 The mercury cycle

In comparison to the other metals, one of the major distinguishing features of Hg is the great extent to which it re-circulates in the environment via the atmosphere. Once emitted mercury is believed to cycle between air, water, soil, and vegetation media. The specific pathway(s) actually taken and the fate experienced by a given mercury species, depend upon many factors; its chemical and physical characteristics, as well as the prevailing environmental and meteorological conditions existing at any given time and place (Schroeder and Munthe, 1998).

Volatilisation fluxes of mercury from natural surfaces should be taken into account when constructing biogeochemical cycles for this element and when calculating mass balances for Hg on local, regional and global scales (Schroeder et al., 1989). Te following section will deal specifically with Hg° since it is the major Hg species involved in extensive environmental cycling.

2.5.1 Air – water exchange

Once entering natural waters predominantly through atmospheric precipitation and dry deposition, Hg° can be transformed into more toxic forms, such as monomethyl and dimethyl mercury. The bioconcentration of these species in seafood represents a health risk to humans. However, the principal form of mercury in waters is the inorganic divalent form, in sea-water stabilized as $HgCl_4^{2-}$ (Olmez and Ames, 1997). One of the most important pathways for the removal of mercury from natural waters is reduction to elemental mercury followed by re-volatilisation to the atmosphere. Although the mechanisms by which this reduction occurs are not well understood, there is evidence for both biological pathways (Mason et al., 1994) and chemical photo-reduction (Brosset, 1987; Munthe and McElroy, 1992).

On a global scale it is estimated (Mason et al., 1994) that the oceans releases ~2000 tonnes of Hg per year, which is in balance with the total deposition flux into the marine environment. Several studies have been performed to investigate the air-water exchange of mercury. In the work by Urba et al. (2000), gas-phase mercury concentrations over the southern Baltic Sea coasts were measured. It was concluded that during the period from mid-June to mid-August (1997) the Baltic Sea served as the main gaseous mercury source in the region. Boudala and co-workers (2000) reported mercury flux over two lakes in Kejimkujik (Nova Scotia, Canada) in the range of 0,7 – 12,5 ng m^{-2} h^{-1}. In both studies mentioned, it was confirmed that emission/volatilisation was enhanced by solar radiation, air temperature and probably wind.

2.5.2 Air – soil exchange

Soils, especially the humus layer of forest soils, are often viewed as a net sink for the Hg pool present in the atmosphere. Mercury binds strongly to organic components constituting the humus (Lindqvist et al., 1984; Johansson et al., 1991). Nevertheless, some volatilisation of mercury does occur, especially from land naturally or anthropogenically enriched in mercury (Ferrara et al., 1998). The work of Schroeder et al. (1989) and Xiao et al. (1991) revealed that Hg was deposited to soil surfaces in the Swedish boreal forest during winter and was emitted or re-emitted during the rest of the year. A consistent theme from recent measurements over soil surfaces is that mercury fluxes are higher over soils exposed to direct solar radiation than over those which are protected from direct sunlight by a forest canopy, and that mercury release is strongly correlated with soil temperature. In measurements made at background sites in Tennessee, USA, soil mercury fluxes averaged between 2 and 7 ng m^{-2} h^{-1} over forest soil and between 12 and 45 ng m^{-2} h^{-1} over open field soil. There are substantial variations of the magnitude of volatilisation fluxes depending on the type of soil or solid waste deposit considered. The annual global emission of Hg from soil had been estimated to ~1000 tonnes (Carpi and Lindberg, 1998).

2.5.3 Air – vegetation exchange

The potential importance of air-vegetation exchange in the geochemical cycling of mercury is now being recognized. However, at the time being there is no estimate of the Hg pool currently residing in plant biomass globally or on a regional basis, even though the amount involved could be quite significant in environmental budgets. Since 1979, various research groups have made geographically restricted studies on uptake and/or emission of Hg from different types of vegetation (Schroeder and Munthe, 1998). In a more recent study performed by Lindberg and co-workers (1998) concentration gradient measurements were made over forest canopies in the deciduous forest of Walker Branch Watershed (south-eastern USA), over a pine plantation distant from Oak Ridge (south-eastern USA), over laboratory tree seedlings, over forest floor vegetation in a remote boreal forest watershed in Sweden, and over wetland vegetation in Florida. Results from all these sites indicate the existence of bi-directional Hg° fluxes. Deposition events occurred during about 40% of the measurement period, which suggests that (re-)emission/volatilisation may be the dominant flux direction. The actual source of the Hg° emitted from vegetation is unclear, but Lindberg and co-workers (1998) hypothesized that it mainly stems from gaseous Hg° in soil pores, which can both have truly natural and anthropogenic origin. This transpiration of mercury represents a previously unmeasured mobilization of Hg° from the continents to the troposphere. This affects the total residence time of mercury and enhances its capability to long-range transport and conversion to more reactive and toxic species.

2.6 Atmospheric mercury

Mercury is one of the most important trace elements emitted to the atmosphere due to its toxic effects on the environment and human health, as well as its role in the chemistry of the atmosphere (Pacyna and Pacyna, 2000). Gaseous mercury is well mixed in the troposphere with background concentrations of ~1-4 ng m^{-3} (Slemr and Langer, 1992). Atmospheric Hg equilibrates among gaseous, aqueous and solid/particulate phases (Lin and Pehkonen, 1999) and is subjected to a variety of physical and/or chemical or photochemical processes and interactions (Schroeder and Munthe, 1998). Elemental mercury makes up ~95% of the total gaseous mercury in the atmosphere in unpolluted areas, whereas oxidized forms and particulate associated mercury only constitute a few percent. However, TPM and GDM are of interest because of the higher deposition rates of these species (Ebinghaus et al. 1994; Slemr et al., 1985; Lamborg et al., 1995). Traces of methyl mercury forms are also present in air (Fitzgerald et al., 1991).

2.6.1 Transport

Atmospheric transport and dispersion of mercury are considered to be an environmental phenomenon on global, regional and local scales (Schroeder and Munthe, 1998). The findings of elevated Hg concentrations in remote lakes are explained by atmospheric input, and hence is one of the detrimental effects of this element’s ability for long-range transport (Lamborg et al., 1995). The elemental form of mercury is relatively unreactive and has a high volatility and low solubility in natural waters, which imparts a long atmospheric residence time of 6 to 24 months (Slemr et al., 1985; Lindqvist and Rodhe, 1985). Hence, Hg° is likely to be transported over very long distances, commonly tens of thousands of kilometers. Divalent mercury species in the gas phase are likely to be removed in the vicinity of a few tens to a few hundreds of kilometers from their sources. Particulate mercury species are likely to be deposited at intermediate distances, depending on aerosol mass/diameter (Schroeder and Munthe, 1998).

2.6.1.1 Local patterns

According to Mason and co-workers (1994) about half of the anthropogenic Hg emissions appear to enter the global atmospheric cycle whereas the other half is deposited locally. This is confirmed by the pronounced gradients of Hg concentration found with increasing distance from point sources (Keeler et al., 1995).

2.6.1.2 Regional patterns

A few studies have been designed to identify spatial Hg gradients in regional and global settings. In a network of eight sites across the Nordic countries, sampling of Hg in precipitation (wet deposition and Hg_{part}), and Hg° on Au-traps were undertaken. It revealed an increase with a factor of three in the annual wet deposition of Hg towards the southwestern part of the region, which is closer to probable source areas on the European continent (Iverfeldt, 1991). Steinnes and Andersson (1991) studied the atmospheric deposition of mercury by the analysis of moss samples from 500 sites regularly distributed over Norway. Having no root system, mosses depend on uptake of chemical substances from above and are regarded as a medium depicting relative wet deposition patterns fairly well. The results from this work were in agreement with Iverfeldt (1991) as far as the southern areas of Norway were concerned, but the values for central and northern part of the country were elevated not depicting the north-south gradient explicit in Iverfeldt’s study. Steinnes and Andersson suggested that dry deposition of mercury makes up a significant portion of the airborne Hg settling at northern latitudes. This is coherent with Iverfeldt's measurements of gas and particulate Hg. These values were relatively uniform for the Nordic countries, the annual average of Hg° for the southern site (3.2 ng m^{-3}) being only 15% higher than the central and northern site average (2.8 ng m^{-3}). Annual means of total particulate mercury (TPM) varied even less between these sites. Still, episodic events with higher gaseous and particulate mercury concentrations occurred more frequently in the southern site, which was nearest to continental source areas (Iverfeldt, 1991). The uniform Hg_{part} data in the study by Iverfeldt (1991) may be explained by gas-to-particle conversion processes or local emission sources of particulate Hg. Anyhow, the data are limited (only two stations) and do not allow any firm conclusions to be drawn.

2.6.1.3 Global patterns

In 1977-1980, 1990 and 1994 Slemr and co-workers measured the latitudinal distribution of atmospheric mercury over the Atlantic Ocean. The results of these measurements showed a pronounced concentration gradient between the northern (1990: 2.25 ng m^{-3}) and southern hemispheres (1990: 1.50 ng m^{-3}). This is probably due to elevated burdens of the north when it comes to industrialization and population. Within the northern hemisphere the TGM concentration increased with increasing latitude to up to 55°N (corresponding to central Europe) and then decreased further north. No such gradient was found within the southern hemisphere (Slemr et al., 1985; Slemr and Langer, 1992; Slemr, 1996).

2.6.1.4 Removal mechanisms

The major removal mechanisms for atmospheric mercury are wash-out of airborne particulate and oxidized forms, aqueous oxidation of elemental mercury to more water-soluble forms, and dry deposition (Pleijel and Munthe, 1995). The dominating process is dependent on the individual concentrations of the different mercury species, the presence of other atmospheric constituents involved in the removal process (e.g. aerosols, ozone) and the type of land use/cover/surface. For instance, the work by Steinnes and Andersson (1991) indicates that dry deposition is a more important removal process at northern latitudes than in southern areas. Studies of mercury fluxes in forested areas suggest that dry deposition is of equal or greater importance than wet deposition (Schroeder and Munthe, 1998).

2.6.2 Atmospheric reactions

Both gaseous- and aqueous-phase processes are potentially important for the overall atmospheric cycling of mercury (Schroeder and Munthe, 1998). But many of the major red-ox reactions involving mercury are assumed to take place in the aqueous phase, such as fog droplets (Pleijel and Munthe, 1995). Elemental mercury will pass through the droplet surface until an equilibrium concentration is established according to Henry's law. Hg°(aq) will be oxidized to Hg(II) by ozone (O_3), and other oxidants, and form complexes according to the chemical composition of the droplet.. Henry's law constants for various Hg species are listed in Table 2.

*Table 2: Gas-liquid equilibrium and Henry's law constants for mercury compounds of interest**

Equilibrium	H (M atm^{-1})
Hg° (g) ⇔ Hg° (aq)	0.11
$Hg(OH)_2$ (g) ⇔ $Hg(OH)_2$ (aq)	1.2×10^4
$HgCl_2$ (g) ⇔ $HgCl_2$ (aq)	1.4×10^6
CH_3HgCl (g) ⇔ CH_3HgCl (aq)	2.2×10^3
CH_3HgCH_3 (g) ⇔ CH_3HgCH_3 (aq)	0.13

* T = 25 °C.
Source: Lin and Pehkonen (1999).

At the present, the identified transformation pathways of atmospheric mercury include gaseous and aqueous phase oxidation of Hg°, e.g. by O_3, aqueous reduction by Hg(II) by sulphite (SO_3^{2-}), aqueous phase oxidation of Hg° by hydroxyl radical ($^{\bullet}OH$), aqueous phase reduction of Hg(II) by hydroperoxyl radical ($HO_2^{\bullet}$), aqueous phase oxidation of Hg° by chlorine ($HOCl/OCl^-$), gaseous phase oxidation of Hg° by chlorine (Cl_2) and gaseous phase oxidation of Hg° by nitrate radical ($NO_3^{\bullet}$) (Lin and Pehkonen, 1999). The reaction equations are listed in the following paragraphs.

2.6.2.1 *Oxidation of Hg° by O_3*

Oxidation processes of Hg° involving ozone have been identified in the gas phase. Elemental Hg may react with O_3 to form either HgO (g) or HgO (s) (Schroeder et al., 1991; Hall, 1995).

$$Hg°(g) + O_3\,(g) \rightarrow HgO\,(g) + O_2\,(g) \tag{1}$$

$$Hg°(g) + O_3\,(g) \rightarrow HgO\,(s) + O_2\,(g) \tag{2}$$

Hall (1995) found that sunlight irradiation increases the rate of this reaction six-fold, although it is not clear what causes this increased rate. Ozone has also been shown to oxidize Hg° in aqueous solutions. This is probably the major removal mechanism for Hg° in the atmosphere, especially in the presence of clouds or fog (Munthe, 1992; Pleijel and Munthe, 1995). Hg(II) is formed in this reaction:

$$Hg°(aq) + O_3\,(aq) \xrightarrow{H+} Hg^{2+}\,(aq) + OH^-\,(aq) + O_2\,(aq) \tag{3}$$

Ozone is a daytime oxidant, since it is produced from the photochemical reactions of NO_x and VOC (Finlayson-Pitts and Pitts, 1986). In atmospheric water, ozone mainly origins from the scavenging of gaseous O_3 into the aqueous phase.

2.6.2.2 Oxidation of Hg° by $^{\bullet}OH$

Lin and Pehkonen (1997) suggested the following mechanism:

$$Hg^{\circ}\,(aq) + {}^{\bullet}OH\,(aq) \rightarrow Hg^{+}\,(aq) + OH^{-}\,(aq) \tag{4}$$

$$Hg^{+}\,(aq) + {}^{\bullet}OH\,(aq) \rightarrow Hg^{2+}\,(aq) + OH^{-}\,(aq) \tag{5}$$

The hydroxyl radical is also a daytime oxidant. In atmospheric water, $^{\bullet}OH$ comes either from the scavenging of gaseous $^{\bullet}OH$, or from in-cloud production through the photolysis of ferric-hydroxide complexes (Finlayson-Pitts and Pitts, 1986; Lin and Pehkonen, 1999).

2.6.2.3 Oxidation of Hg° by chlorine ($HOCl/OCl^{-}$)

Depending on pH, aqueous chlorine can exist as two species: hypochlorous acid and hypochlorite ion ($HOCl \leftrightarrow H^{+} + OCl^{-}$, $K_a = 10^{-7.5}$). Both species are capable of oxidising Hg°:

$$Hg^{\circ}\,(aq) + HOCl\,(aq) \rightarrow Hg^{2+}\,(aq) + Cl^{-}\,(aq) + OH^{-}\,(aq) \tag{6}$$

$$Hg^{\circ}\,(aq) + OCl-\,(aq) \xrightarrow{H+} Hg^{2+}\,(aq) + Cl^{-}\,(aq) + OH^{-}\,(aq) \tag{7}$$

Reactive chlorine (Cl_2, HOCl and $Cl^{\bullet}$) is a night-time oxidant and usually reaches its peak concentration just before sunrise (Impey et al., 1997). Before these reactions can take place, Cl_2 must be scavenged into the aqueous phase.

The divalent mercury produced in these reactions is likely to form a number of complexes depending on the ions available in the droplets, Cl^{-}, SO_3^{2-}, and OH^{-} being the most important (Pleijel and Munthe, 1995). Oxidation of Hg° may to some extent be balanced by reduction processes occurring simultaneously in the atmosphere. The aqueous-phase reduction of Hg(II) species by sulphur (IV) has been suggested by Munthe et al. (1991), but probably other reduction reactions also occur, for instance photochemically initiated reduction of Hg(II) species (Schroeder and Munthe, 1998).

2.6.2.4 Reduction of Hg(II) by S(IV)

The aqueous phase reduction of Hg(II) by sulphite was investigated by Munthe et al. (1991). The proposed mechanism involves the formation of an unstable intermediate, $HgSO_3$, that decomposes to produce Hg^{+} which in turn is rapidly reduced to Hg°. It is not clear whether S(VI) is produced during the reduction. The overall chemical scheme can be written as follows (Pleijel and Munthe, 1995):

$$HgSO_3\,(aq) \rightarrow Hg^{\circ}\,(aq) + \text{products} \tag{8}$$

The scavenging of SO_2 (a primary pollutant) into atmospheric droplets forms sulphite. The solubility of SO_2 depends strongly on pH of the droplets and increases with increasing pH (Lin and Pehkonen, 1999)

2.6.2.5 Photoreduction of Hg(II)

The photoreduction of a variety of halide- and organo-Hg(II) complexes is well known. In addition the divalent mercury in $Hg(OH)_2$ complexes can be reduced to Hg° by photolysis:

$$Hg(OH)_2\ (aq) \rightarrow Hg^{\circ}\ (aq) + \text{products} \tag{9}$$

Mercury-chloride complexes dominate the dissolved Hg(II) fraction in competition with the reactive Hg(II)-S(IV) complexes. If pH increases, the importance of $HgCl_2$ will decrease in favour of the Hg(II)-S(IV) complexes which in turn will lead to lowered concentrations of dissolved Hg(II), due to an enhanced production of volatile Hg° via reduction of $HgSO_3$ (Pleijel and Munthe, 1995).

Only a few chemical reactions of mercury in the gaseous phase have been studied in laboratory investigations. This is partly due to experimental challenges associated with performing this kind of investigations. Of the homogeneous gas-phase reactions which Hg undergoes, it is the reaction with ozone (equations 1 and 2) that is most important (Hall, 1995). The following section gives two examples of other reactions involving Hg for which experimental procedures have been published.

2.6.2.6 Oxidation of Hg° by nitrate radical

Sommar et al. (1997) studied the gaseous phase oxidation of Hg° by $NO_3^{\bullet}$. The reaction equation is assumed to be:

$$Hg^{\circ}\ (aq) + NO_3^{\bullet}\ (g) \rightarrow HgO\ (g) + NO_2\ (g) \tag{10}$$

In the atmosphere, $NO_3^{\bullet}$ is mainly produced by the reaction of O_3 and nitrogen dioxide. Since it can be rapidly photolyzed under solar radiation ($\lambda \leq 670$ nm), $NO_3^{\bullet}$ is a night-time oxidant (Finlayson-Pitts and Pitts, 1986).

2.6.2.7 Oxidation of Hg° by hydrogen peroxide (H_2O_2)

Seigneur et al. (1994) suggested the following reaction scheme:

$$Hg^{\circ}\ (g) + H_2O_2\ (g) \rightarrow Hg(OH)_2\ (g, s) \tag{11}$$

H_2O_2 is a daytime oxidant, and is produced by the photooxidation by formaldehyde and hydrocarbons in the presence of NO_x (Finlayson-Pitts and Pitts, 1986).

2.7 Particulate mercury

Particulate mercury is typically found at levels ~ 1-100 pg m^{-3} in ambient air, constituting only a few percent of total atmospheric mercury in background areas. In industrialized regions however, Hg_{part} may constitute 40% of the atmospheric mercury, suggesting that the particulate fraction is largely of anthropogenic origin (Xiao et al., 1991; Keeler et al., 1995; Lamborg et al., 1995). Due to the relatively low background levels of particulate mercury the importance of this species in atmospheric chemistry, transport and deposition of Hg has long been underestimated and largely ignored. However, during the last decade increasing attention has been given to Hg_{part}, as this species, together with water-soluble gaseous divalent mercury, is more effectively deposited than the elemental form. Consequently TPM and GDM are important for the transport and deposition of Hg to the earth's surface.

The amount and particle size of the observed TPM vary dramatically from site to site as well as from day to day. Levels in urban/industrialized areas are reported in the range from 86 to more than 1000 pg m^{-3}, whereas rural values are in the order of 10 to 30 pg m^{-3} (Keeler et al, 1995; Lu et al., 1998; Pirrone et al., 1995). Values for the Mediterranean area are reported to be in the range 10-50 pg m^{-3} (N. Pirrone, pers. comm.). In Polar regions the background level is generally in the range between 1-5 pg m^{-3} (Lu et al., 1998; Berg et al., 2001).

2.7.1 Sources

The sources of particulate mercury are mainly the same as for mercury in general, which are discussed in chapter 2.2. The increased levels of TPM in the vicinity of point sources illuminate the importance of the anthropogenic origin of this species (Ebinghaus et al., 1994; Mason et al., 1994; Keeler et al., 1995). Of particular interest is coal combustion, accounting for 72 of 158 tonnes $year^{-1}$ of total point source emissions in the US. During combustion Hg° (g) is emitted from coal, and in the post-combustion environment a significant fraction is transformed to $Hg^{2+}X$ (g) and Hg_{part}. Fly ash produced in the process will to a great extent adsorb mercury and thereby increase the Hg_{part} fraction (Hall et al., 1995; Galbreath and Zygarlicke, 2000). Waste incineration is also an important source of particulate mercury. Natural sources would typically be volcanoes and erosion of mercury enriched rocks. Studies have revealed that the TPM fraction increases with the amount of total particulate mass in the atmosphere (Keeler et al., 1995), hence, areas polluted with elevated levels of particles will also experience an increased burden of particulate-bound mercury.

2.7.2 What is particulate mercury?

Particles are common significant components of the atmosphere, particularly the troposphere. They consist of an amazing variety of materials and discrete objects that may consist of solids or liquid droplets. Particle diameters may range between ~0.002 μm and ~100 μm, though the lower size range 0.002–10 μm dominates in the atmosphere. Particles are usually divided into two fractions according to their size. The coarse mode consisting of particles with diameters ≥ 2.5 μm are generally comprised of soil elements over the continents and sea salt elements over the ocean. The fine fraction is defined as particles with diameters ≤ 2.5 μm and arise from gas-to-particle conversions and combustion processes (Finalyson-Pitts and Pitts, 1986).

Particulate mercury can be both primary and secondary. The primary portion is introduced into the atmosphere as Hg_{part}, such as combustion aerosols, while the secondary ones are formed after entering the atmosphere through physical and chemical processes such as adsorption, evaporation, oxidation and reduction reactions. These interactions however are not well understood at the time being and need further investigation. The formation and chemistry of Hg_{part} involve heterogeneous reactions taking place both in the gaseous and aqueous phases. Droplets of water are widespread in the atmosphere and fog and clouds represent liquid media for chemical reactions involving particulate mercury to occur.

2.7.2.1 Speciation – operational definitions

A few operationally defined approaches have been undertaken in order to investigate the speciation of particulate mercury. Brosset and Lord (1991) differentiated mercury species in particulate matter based on the different chemical affinities. A solution of $NaBH_4$ was used to extract Hg from airborne particulate matter retained on a quartz wool plug and the released Hg was defined as the $NaBH_4$-reducible fraction. The residual Hg on the quartz wool was determined by pyrolysis analysis at 800 °C and defined as the "un-reducible fraction". The results show that 57-85% of the total particulate mercury was $NaBH_4$-reducible.

For samples of urban particulate matter (SMR 1648, NIST) differentiation of the Hg species, using their thermal desorption properties, has been reported by Lu and Schroeder (1996). The results suggest that 40% of the mercury was released by the time the temperature had reached 180 °C and about 89% by the time the temperature had reached 300 °C. On average, over 90% of the total mercury in the standard reference material (SMR 1648, NIST) was released at a temperature of 540 °C.

Hg_{part} has also been distinguished based on its size distribution. The results indicate great variations from site to site as well as from day to day. In urban Detroit, USA, Keeler and co-workers (1995) found that 60-100 % of the particulate mercury was present in the fine size range (< 2.5 μm). The average particle size in the fine mode was 0.68 μm, while the average in the coarse mode was 3.78 μm. The observation of the coarse particle mode was somewhat unexpected, as other studies suggest that Hg_{part}, being primarily a combustion aerosol, should be submicron in size. The coarse fraction is of importance since the dry deposition flux is 4-5 times greater than the fine particle flux (Pirrone et al., 1995). However, the fine fraction, having a longer residence time, is liable to be transported over long distances.

2.7.2.2 Speciation – chemical composition

Seigneur and co-workers (1998) have undertaken studies to assess the extent to which mercury may adsorbe to particulate matter in the atmosphere. It was found that mainly divalent Hg species adsorb to aerosols, while adsorption of Hg° appeared to be negligible. The reactions involving Hg_{part} took place in both gaseous and liquid media in ambient air. Experiments conducted with rainwater suggest that a substantial fraction of the dissolved Hg species (such as $HgCl_2$ and $Hg(OH)_2$) is present in the particulate phase. Hg_{part} is assumed to form as mercury complexes adsorb onto particles within the droplet. It was concluded that one fraction of TPM consists of Hg species, such as $HgCl_2$, $Hg(OH)_2$, which are adsorbed to particles, another fraction is made up of solid mercury compounds (at ambient air temperature), such as HgO and HgS.

The chemical composition of atmospheric particles varies and the knowledge on which properties that enhance adsorption of mercury is limited. However there is strong evidence that especially soot particles (i.e. elemental carbon particulate matter) have a strong tendency to adsorb mercury species (Pleijel and Munthe, 1995; Petersen et al., 1995), especially the divalent compounds. Such adsorption may appear within cloud or rain droplets but there is also evidence of gas-phase adsorption of mercury to carbon particles. The elemental carbon concentration in ambient air is assumed to be 0.5 $\mu g\ m^{-3}$. Cloud and rain-water contain 15-300 $\mu g\ l^{-1}$ (Seigneur et al., 1998).

The knowledge of the chemical speciation of Hg_{part} is limited and further investigation is needed. Currently the understanding of the interaction of Hg species with soot and atmospheric particulate matter in the gas and aqueous phases is limited by the lack of basic research data on the subject. Future work should address the speciation of Hg present in particulate matter (e.g. HgO, HgS, or dissolved/volatile species such as $HgCl_2$ or $Hg(OH)_2$). In order to obtain quality data of Hg_{part} under atmospheric conditions it is imperative to have access to reliable methods for sampling and analysis.

2.8 Atmospheric mercury in the Arctic

The high level of mercury contamination observed in the once pristine Arctic environment is largely connected to the unique properties of mercury as a metal, including its long residence time and potential for long-range transport. The annual average of gaseous mercury in Arctic areas is ~1.5 ng m^{-3} (Schroeder et al., 1995; Berg et al., 2001). This concentration is three times higher than the values reported by De Mora et al. (1993) for Antarctica and is probably explained by heavier industrialization of the northern hemisphere. A study by Berg et al. (2001) modelling the Hg contribution to Spitsbergen from source areas in central and northern Europe concluded that the direct atmospheric transport of Hg° from these areas is small and that the level has to be seen in relation to a global or hemispherical scale. A more extensive calculation made by Lin et al. (2001), considering the northern hemisphere, identified Siberia, Europe and North America as the main source regions of Hg found in the Canadian Arctic. This work further concluded that long-range transported Hg dominates at autumn and winter, whereas the sources seem to be local at summertime.

At Ny-Ålesund the background level for particulate mercury is reported to be in the range 1-5 pg m^{-3}, constituting less than 0.2% of the average Hg° concentration at this site (Berg et al., 2001). GDM concentrations were measured for the first time during spring 2000 at Ny-Ålesund (Valdal, 2001) but regular sampling in Alaska since spring 1999 revealed background levels for GDM close to the detection limit (< 2.0 pg m^{-3}) (Lindberg et al., 2000).

2.8.1 Arctic – a sink for atmospheric mercury?

Since mercury, unlike all the other heavy metals, exists predominantly in the vapour phase in the atmosphere, it may be more appropriate to look to volatile or semi-volatile persistent organic pollutants for model compounds for the purpose of predicting the atmospheric behaviour of Hg°. In the case of semi-volatile organic compounds such as PCBs, HCB and organochlorine pesticides (e.g. HCHs, DDT, chlordane, toxaphene) there exist strong scientific evidence that these chemicals participate in a “global distillation” phenomenon (Mackay et al., 1986; Schroeder and Lane, 1988; Kurtz, 1990; Wania and Mackay, 1996). This trend effectively transfers chemical emissions from equatorial/tropical or subtropical and temperate regions of the earth to the polar regions via the so-called “grasshopper effect”. It is reasonable to assume that mercury exhibits similar environmental behaviour. The warm and humid conditions in the tropical and subtropical regions enhance the volatilisation, emission and re-emission of such substances to the atmosphere. The atmosphere, in turn, constitutes an efficient medium for their dispersal and systematic accumulation in colder climates (Schroeder and Munthe, 1998). The tendency of mercury to “accumulate” in cold climates is suggested in a study by Steinnes and Anderson (1991).

2.8.2 Seasonal variations

Concentrations of TGM at Alert, Canada, were registered in the range 0.7 – 2.9 ng m^{-3} during 12 months (8/92 – 8/93). In 1995 high temporal resolution measurements revealed even lower values (0.2 – 2.9 ng m^{-3}) for certain time periods. The peak Hg° concentrations were observed during summer, probably due to temperature and/or sunlight induced emissions/re-emissions from the earth's surface during this time of year, and not solely due to atmospheric transport from any specific sector with large mercury emissions (Schroeder et al., 1997; Berg et al., 2001). During autumn and winter the TGM levels were relatively constant with concentrations between 1.0 and 2.0 ng m^{-3}. At springtime however atmospheric mercury behaved rather peculiarly.

2.8.3 Depletion episodes

The implementation of high-resolution measurements of Hg° at Arctic research sites has revealed a new phenomenon. During the three-month period following polar sunrise in March (at Ny-Ålesund), episodes are observed where Hg° concentrations decrease below 1 ng m^{-3} and frequently beneath the detection limit of the detector (0.1 ng m^{-3}). These depletion events coincide with the depletion of ground level ozone, which have been registered since the late 80s (Solberg et al., 1996). Figure 1 shows high-resolution measurements of elemental mercury and ozone following polar sunrise (March – May, 2000) at the Zeppelin Mountain, Ny-Ålesund.

The depletion of TGM was first observed in the Canadian Arctic in 1995 (Schroeder et al., 1998). More recent measurements made in Barrow, Alaska (Lindberg et al., 2000) and Ny-Ålesund, demonstrate that this is not simply a local occurrence at Alert. The phenomenon is probably caused by the specific chemical and physical conditions in the atmosphere following polar sunrise. It is suggested that elemental mercury is oxidized to more reactive species like TPM and GDM and preliminary measurements at Arctic locations support this theory (Lu and Schroeder, 1998; Lindberg et al., 2000; Valdal, 2001). Gaseous divalent mercury and particulate mercury have elevated deposition rates compared to vapour phase mercury and hence contribute increased concentrations of this toxic element to terrestrial and aquatic ecosystems at a time of year when biota is preparing for peak summer time activity. This may explain the increased concentrations observed in Arctic sediments, biota and wildlife (Schroeder et al., 1997).

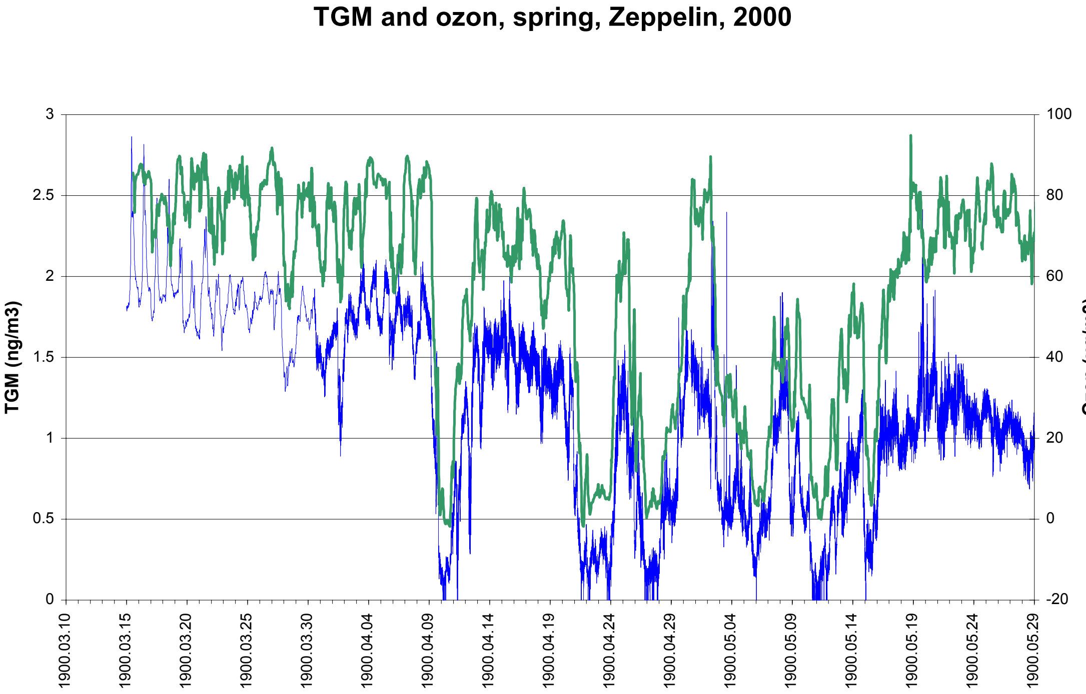

Figure 1: Elemental mercury (blue) and ozone (green) during the period after polar sunrise at the Zeppelin Mountain, Ny-Ålesund, year 2000 (Berg, 2001)

2.8.3.1 Oxidation reactions

The strong correlation with ozone concentrations suggests that mercury depletion episodes are subjected to reactions similar to those, which destroy tropospheric ozone. Being known to scientists for more than a decade, the research on low ozone episodes is more mature compared to mercury depletion events. During polar dawn the ozone concentration may drop from a background level of 65 µg m^{-3} to below the detection limit (about 2 µg m^{-3}) in the matter of hours. Early on, elevated levels of bromide during the periods in question were found to be an explanation of ozone depletion. It was proposed that Br was produced by photolysis of bromoform ($CHBr_3$), which is emitted from algae in the Arctic Ocean and has been seen to accumulate over polar ice during winter (Bottenheim, 1990). Heterogeneous gas/solution reactions at the interface of hygroscopic sea salt aerosols may also be a source of airborne reactive Br. Several of these species have the potential to oxidise Hg° to Hg(II) compounds (e.g. BrO, BrCl) (Lindberg et al., 2000).

Many of the compounds arising from reactive Br exhibit a strong diurnal pattern, indicating the importance of sunlight and photochemical reactions (Vogt et al., 1996). In a study located on the Zeppelin Mountain, Ny-Ålesund, Solberg and co-workers (1996) found lower concentrations of several individual hydrocarbons during episodes of ozone depletion. This suggests that chlorine is a significant oxidant of ozone as well. The role of chlorine for the chemistry of mercury however is not well established. Solberg et al. (1996) also studied the role of meteorological parameters on ozone concentrations. On the basis of trajectory calculations they found that low ozone episodes predominantly occurred when the air masses were transported from west or north. This was consistent with the assumption that these processes take place over the Arctic Ocean. Further, the episodes were associated with a cold boundary layer beneath a thermally stable layer, suppressing mixing with the free troposphere.

3 Methods for the sampling and determination of TPM

3.1 Sampling of particulate mercury

Since particulate mercury was identified and became a desired species to determine, several methods for sampling and analysis have been applied and evaluated. Filter packs, quartz wool plugs, liquid bubbler/impingers, impactors and a denuder-based methods are among the reported devises used for sampling airborne particulate matter in ambient air. The general sampling set-up consists of a particulate trap, a pump actively sucking air through it and a gas meter for the registration of the sampled air volume. An introduction to the various particulate trapping methods follows.

3.1.1 Wool plugs, liquid bubblers and impactors

Practice of these methods is reported in the literature. However, due to various limitations the application is not extensive for the sampling of particulate mercury.

3.1.1.1 A liquid bubbler/impinger

Total gaseous mercury, including gaseous and particulate mercury, was trapped in an acidic solution by bubbling air through it. The trapping efficiency was reported to be better than 95%. The concentration of particulate mercury was determined as the difference between the total atmospheric mercury and gaseous-phase mercury (Brosset and Lord, 1991). To obtain a reliable result, it is required that the ratio $[Hg]_{TPM}/ [Hg]_{TGM}$ is not too small. However, the concentration of TPM in ambient air is generally only a few percent of total gaseous mercury (Lu and Schroeder, 1999).

3.1.1.2 Glass/quartz wool plugs

Glass/quartz wool plugs are normally arranged in holders with lower cross-section (a few mm) compared to filter holders, hence the flow rate through the plugs is usually limited to a few litres per minute. The great advantage with this method is the minimum of sample handling steps required. Therefore the risk of contamination is reduced. However, not being entirely inert and having a large surface area, quartz wool has been found to adsorb gaseous elemental mercury and dimethyl mercury (Brosset and Lord, 1991; Lu and Schroeder, 1999). The results when using quartz wool plugs may therefore be biased high for Hg_{part} (Ebinghaus et al., 1999).

3.1.1.3 Impactor

In an impactor the air stream is accelerated by drawing it through one or more converging nozzles or slots. While larger, high inertia particles are unable to follow the undulating air stream and thus impact against the collection surface, the smaller particles follow the air stream and can either be directed to another impactor stage or collected on a filter. A multiple stage impactor is used when size distributions of particles are studied (Keeler et al., 1995). Major disadvantages of this method include “bounce-off”, re-entrainment, wall losses, cross-sensitivity, lack of discreteness (in particle classification), and being labour-intensive (Lu and Schroeder, 1999).

3.1.2 Filter methods

The filtration method is the most widely used and is based on passage of sample air through a filter substrate. Filters remove the particulate phase from the gaseous phase by a combination of five processes: interception, internal impaction, diffusional deposition, electrical attraction and gravitational attraction (Davies, 1983). Polypropylene, paper (cellulose), teflon, glass and quartz fiber are filter materials used for particulate Hg sampling. When considering inertness towards atmospheric components, minimum blank values (easy to clean) and high tensile strength (allowing high flow rates), quartz fibre filters seem to be the best alternative (Lu and Schroeder, 1999). However, glass fibre filters are also a good option and are significantly cheaper than quartz. For sampling, filters can be installed in filterpacks, (47 mm or larger), or in other custom-made devices such as the so-called TPM-trap.

3.1.2.1 Artefacts

According to Lu and Schroeder (1999), determination of particles associated with airborne particulate matter by sampling on filters may be suspect for a couple of reasons. First, some weakly bound/volatile species of Hg on the particles may be "blown off", or evaporated along with water from aqueous aerosols, when air is continuously pulled through the filter during the sampling step. Secondly, since the particles collected on the filter surface will be in extended contact with a large volume of air containing a relatively high level of gas-phase mercury, some gaseous mercury may be adsorbed by the particles retained on the filter. The relative contribution of these processes to the measurement of particulate mercury is still unknown.

3.1.2.2 The TPM-trap – a device for sampling particulate mercury

Recently a new filter-holder for sampling particulate mercury has been developed by Julia Lu (1998) at Environment Canada. This TPM-trap consists of a miniature quartz tube containing a quartz fibre filter disc. The all quartz construction of this device enables it to be easily cleaned by heating at 500-850 °C before sampling. For analysis it is put directly into an analytical train, hence several sample handling steps between sampling and analysis are eliminated (Lu et al., 1998; Lu and Schroeder, 1999). The construction and procedure of the TPM-trap method is thoroughly described in the experimental section in this work.

3.2 Sample preparation

3.2.1 Wet digestion

When conventional filter methods are used, particulate mercury is usually liberated from the sample matrix using one or more oxidizing agents in an acidic medium. Reagents which have been used in the wet digestion of airborne particulate matter for Hg determination, are HF, HCl, H_2SO_4, HNO_3 and $KMnO_4$. The wet digestion procedure is generally followed by a step called cold vapour procedure. The oxidized sample with all mercury species converted to the divalent state is now added a reducing agent, normally tin(II)chloride ($SnCl_2$) or sodium tetrahydroborate ($NaBH_4$). Hence, the Hg^{2+} is reduced to $Hg°$ which is liberated from the sample solution by aeration. From this stage it can either be directly transferred into to the sample cell of a detector, or be pre-concentrated on a gold trap before being thermally desorbed for analysis.

3.2.2 Dry pyrolysis

Pyrolysis is defined as heating the sample to a high temperature. It has been shown that all Hg species will be thermally desorbed from a sample and converted into the elemental form (by pyrolysis) at a temperature of 900 °C (Wang et al., 1995). Probably lower temperature is sufficient since on average, over 90% of the total mercury in standard reference material (SMR 1648, NIST) is released at a temperature of 540 °C (Lu and Schroeder, 1996).

In the case of the TPM-trap, the trap with the sample is put directly into an analytical set-up, and the procedure of dry pyrolysis converts the Hg into the elemental form, which volatilises and is carried further down the analytical line for detection. Only a period of 1-5 minutes is required for the total release of Hg from the sample. Compared with the wet-digestion procedure, pyrolysis is much more rapid and in addition the risk of contamination is reduced, as no sample preparation steps between sampling and analysis are needed.

3.2.3 Pyrolyzer

During the initial stage of the development of the TPM-trap method, the occurrence of two peaks were often observed when analysing samples, especially when a relatively long sampling time (>1 day) was used. It was assumed that this phenomenon could be due to incomplete conversion of mercury species. Compounds such as CH_3HgCl, CH_3HgCH_3 and $HgCl_2$ can be adsorbed by gold, but only Hg° may diffuse into the gold mesh. As the analytical gold trap is heated, the adsorbed species may be released prior to the amalgamated Hg° and result in a double peak pattern. A tube filled with granular magnesium oxide was installed subsequent to the TPM-trap and kept at 900 °C. The aim was to lengthen the high-temperature zone to see if this could effectuate total conversion of the Hg species into the elemental form. Several tests demonstrated a positive effect, the first peak was eliminated and even samples made for longer than 62 hours gave one single peak (Lu et al., 1998). The prolonged pyrolysing effect of the MgO tube can also be achieved with a quartz tube filled with broken bits of quartz (Wang et al., 1995; I. Wangberg, pers. comm.).

3.3 Detection of particulate mercury

Predominantly spectroscopic methods such as atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS) are used for the determination of particulate mercury (and mercury in general). Other methods such as neutron activation analysis (NAA), particle induced x-ray emission (PIXE) (Hacon et al., 1995) and inductively coupled plasma (ICP) (Costley et al., 2000) with various sample introduction methods, have also been employed for the analysis of Hg samples. Only AAS and AFS will be further considered here.

3.3.1 Spectrometric methods

The flexibility, sensitivity and cost-effectiveness of spectrometric methods, in conjunction with wet-digestion/amalgamation or dry pyrolysis/amalgamation, are the basis for the extensive use of these methods for the determination of mercury species. The sample converted to Hg° vapour in the pre-detection steps is irradiated with UV-light at the specific resonance wavelength of mercury (254 nm). In AAS the energy absorbed when the analyte Hg atoms are excited is measured, whereas in AFS the radiation emitted when the excited Hg atoms return to their ground state is measured. Consequently, in AAS a relatively small decrease in a comparatively large electronic signal is measured. AFS detects a small positive signal on the top of a near-zero background signal. Since, technically, it is much easier to measure a small signal relative to “zero” than it is to measure a small difference in a large signal, AFS is capable of achieving a significantly lower detection limit than AAS (Lu and Schroeder, 1999).

Because mercury has got such a high vapour pressure, Hg-samples can be analysed without the use of an ionising flame. Thus the methods are referred to as cold vapour atomic absorption spectroscopy and cold vapour fluorescence spectroscopy (CVAAS and CVAFS respectively) (Olmez and Ames, 1997).

3.4 Sampling and determination of gaseous elemental mercury (TGM)

Amalgamation is the predominant principle for both sampling and determination of elemental gaseous mercury. When sampling Hg°, air is drawn through a tube containing gold either in the form of a wire, metal wool or a thin film coated on the inner wall. The gaseous elemental mercury is retained as it amalgamates with the gold material. The collector is subsequently taken into a laboratory where the Hg° is released by thermal desorption. The sample is either led directly into the detector or is pre-concentrated on a similar gold trap before analysis. Today modern monitors are developed where all these procedures are put together for the automatic sampling and determination of gaseous elemental mercury.

4 Experimental section

Chemicals, reagent procedures, materials and instruments employed in the field and laboratory work are listed in Appendix 1.1 - 1.3

4.1 TPM-trap: a new device for sampling total particulate mercury

Figure 2 shows the custom-built TPM-trap containing the quartz fiber filter disk.

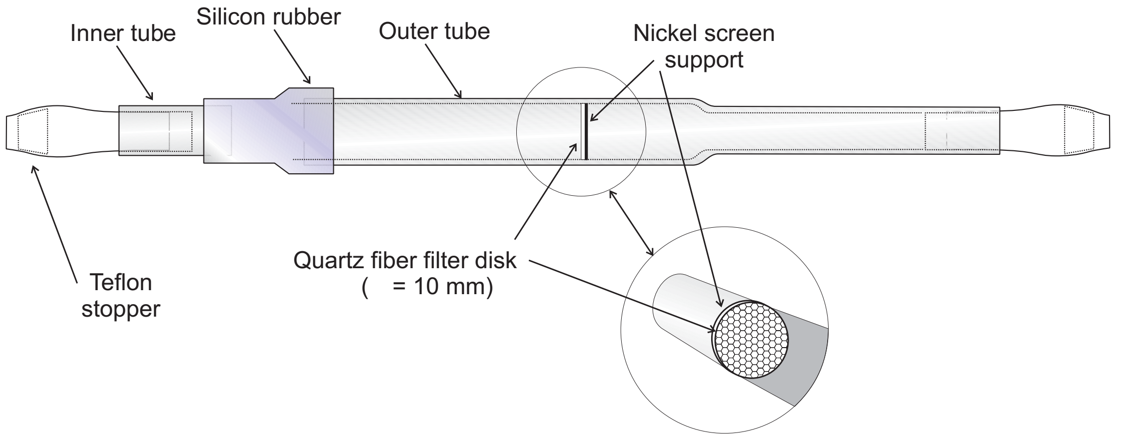

Figure 2: TPM-trap with a quartz fiber filter disk (ϕ = diameter)

Two miniature quartz tubes, one with outer diameter of 10 mm, the other with outer diameter of 13 mm, placed one within the other, are held together by a piece of silicon tubing (inner/outer diameter: 9/13 mm). The conjunction of the tubes holds a filter disk, 10 mm in diameter, cut out from a quartz fibre filter sheet (Munktell 360, pore size: 0.3 µm). The filter disk is supported by a nickel screen support (10 mm in diameter).

4.2 The construction of a sampling line

Figure 3 shows a schematic presentation of the sampling line for collecting particulate mercury.

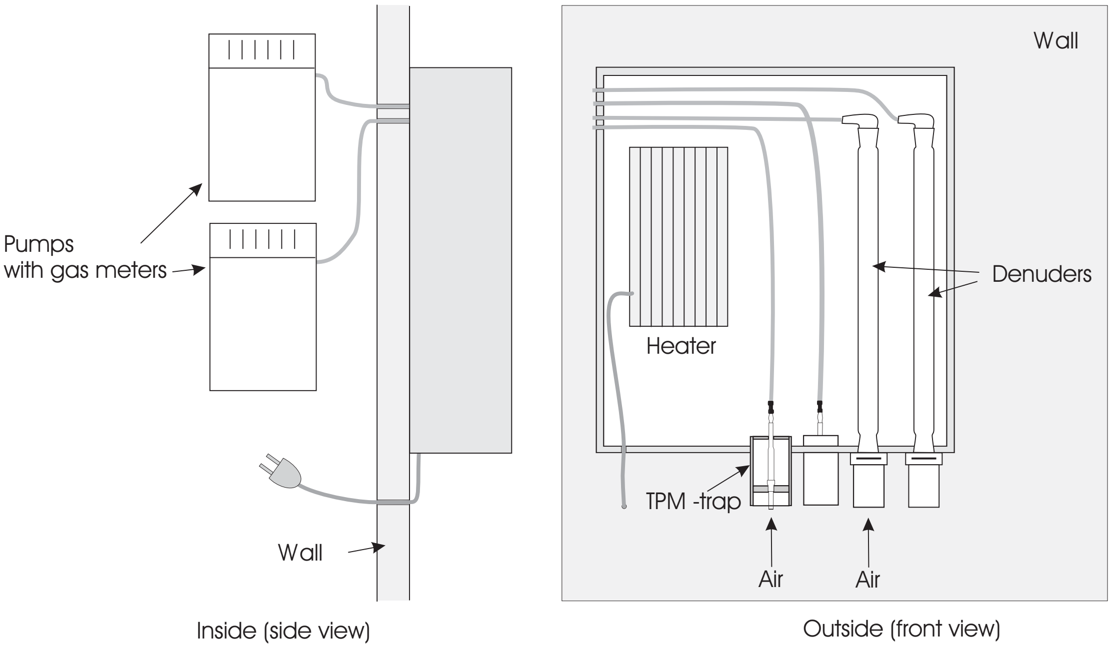

Figure 3: A schematic set-up for sampling Hg_{part}*, side and front view*

To execute outdoor sampling, the TPM-traps were installed in a custom-made box of plywood. This box was developed in collaboration with the Department for Instruments and Field Sampling at NILU (I-Lab). It was constructed to contain two sampling lines (parallels) for TPM-traps and two sampling lines for denuders (GDM) and could be erected on a wall or on a pole. The box contained a small oven to keep the temperature within the box at approximately 10 °C. Within the box the TPM-traps were connected vertically to a set of polyethylene tubing, with the lower end of the traps poking out of holes at the bottom of the box. Approximately ¾ of the trap was in contact with ambient air (at the exterior of the box), only sheltered against wind and precipitation with a polyethylene protection cap. Two traps may be installed at the same time, positioned 5 cm from each other. A detailed description of the sampling box is presented in Figure 4.

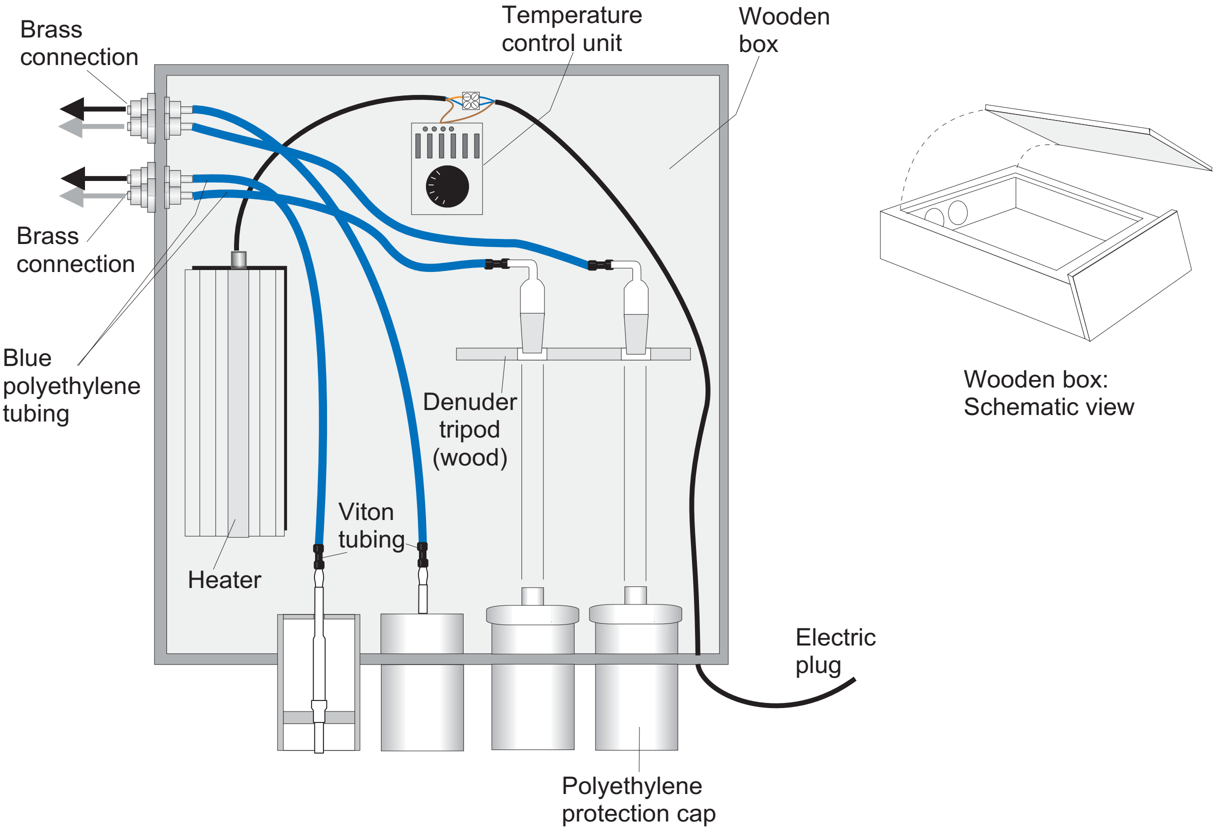

Figure 4: The sampling box with TPM-traps and denuders for the sampling of TPM and GDM.

Air was pulled through the traps using pumps placed indoor. The traps were connected to the pumps via sampling tubing (polyethylene). Gas meters placed upstream of the pumps logged the volumes of air pulled through the traps. A pump positioned downstream of a gas meter is shown in Figure 5.

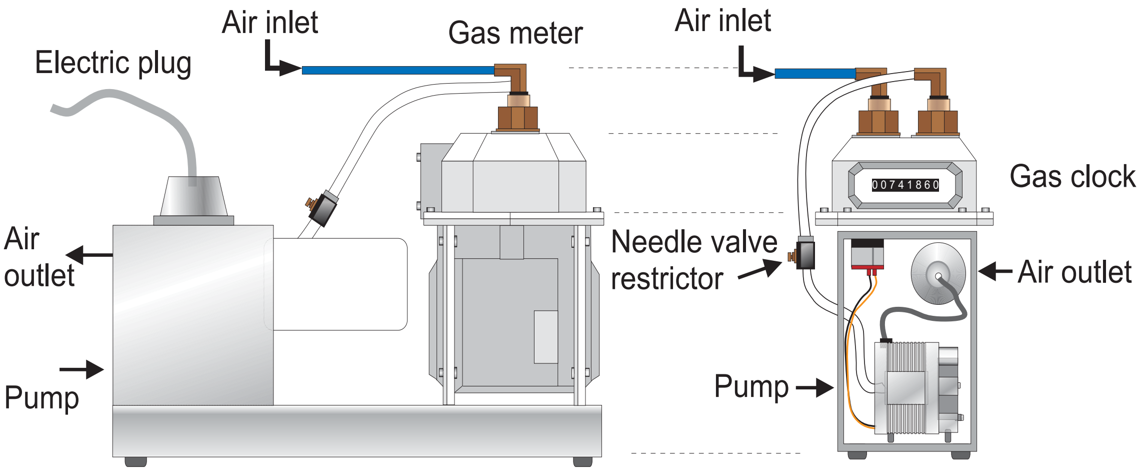

Figure 5: Gas meter and pump, side and front view

4.3 The construction of an analytical system

Figure 6 presents a schematic set-up of the analytical train for the determination of particulate mercury.

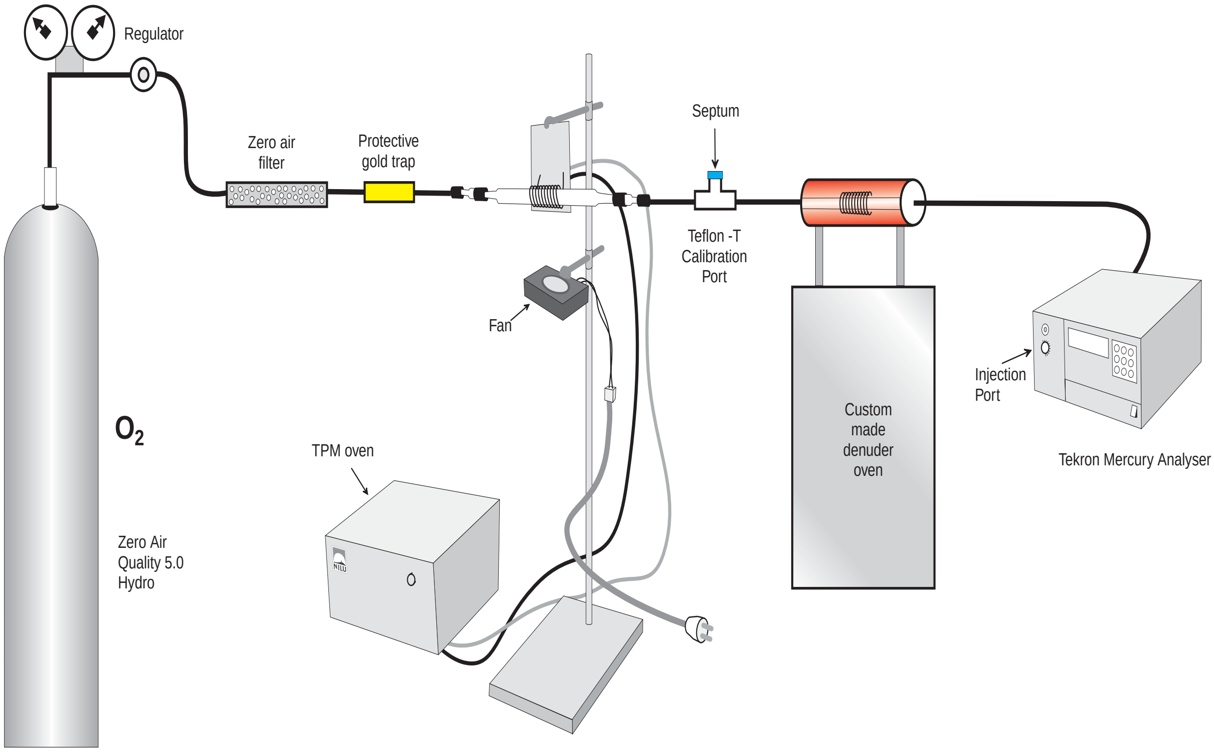

Figure 6: Experimental set-up for total particulate mercury determination

4.3.1 An oven for the particulate traps

A custom-made oven for heating TPM-traps to approximately 900 °C was constructed in collaboration with I-Lab. This thermal installation consisted of a heating coil shaped into a spiral with a diameter of 13 mm fitting the TPM-trap, a voltage source (transformer), and a time regulation. A fan was positioned at adequate distance underneath the heating wire. Both objects were held in place by a stand of clamps. The box containing the transformer and time regulation was positioned on the floor. The set-up is shown in Figure 7. The oven could be adjusted to perform heating between one and twelve minutes (the constituents of the TPM oven are listed in Appendix 1.4).

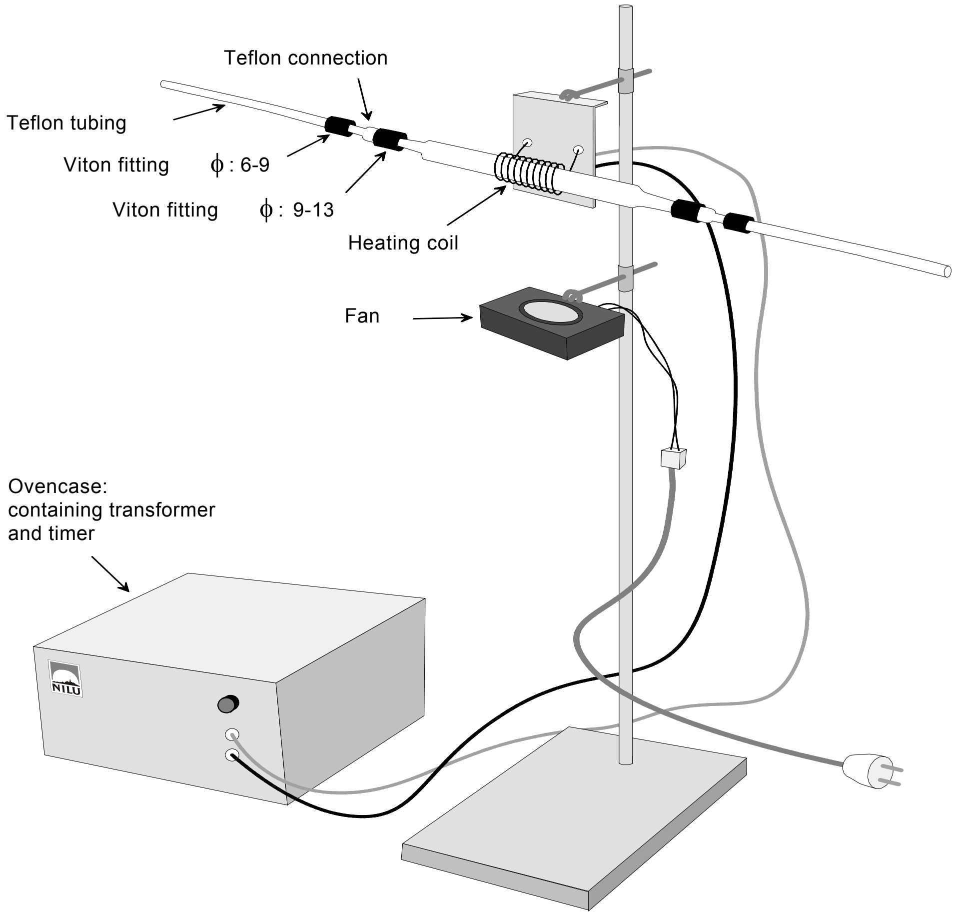

Figure 7: TPM oven (ϕ = diameter)

4.3.2 Pyrolyzer

The pyrolyzer was situated upstream of the TPM heater in the analytical train. It consisted of a 150 mm long quartz tube (inner/outer diameter: 5/7 mm), filled with broken pieces of quartz glass, kept at a constant temperature of approximately 900 °C. The temperature could be obtained by:

1: using the existing two-oven system for the conventional determination of Hg° sampled on gold trap.
2: applying the pyrolyzer unit/oven on the custom-made denuder oven system developed at I-Lab[1].

The second alternative proved to be advantageous as this heater could keep the temperature of the pyrolyzer at a constant level of 900 °C. The first option had some limitations as the two ovens, one for the pyrolyzer and the other for the analytical gold trap, had interrelated electronics, with the result that they could not be heated at the same time. Thus, the pyrolyzer was turned off when the analytical oven was heating. The pyrolyzer as part of the denuder oven is shown in Figure 6. The first option will not be further explained.

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[1] Refer to Valdal, 2001 for a detailed description of the custom-made denuder oven.

4.3.3 A preconcentration step

After the mercury was thermally desorbed off the TPM-trap and transported by carrier gas through the pyrolyzer, the next step was an analytical gold trap, which retains Hg° by amalgamation. When sufficient time had passed, this analytical trap was heated to 450 °C and thereby releasing the elemental mercury in one concentrated lot, which was then transported through the detector for exact determination. (In the case of the AFS detector, the analytical gold trap is located outside the very instrument. When it comes to the GARDIS and TEKRAN, these instruments are monitors and hence the gold adsorbents are located within the instruments. See below).

4.3.4 Detectors

Three detectors were tested/used. Originally, the intention was to employ the MERLIN detector, an atomic fluorescence spectrometer (CVAFS), which was installed at the clean-room laboratory at NILU. Another option available was the GARDIS[2], which detected Hg° by atomic absorption spectrometry (CVAAS). This was the only mobile detector unit, and was also used for the analysis of GDM samples. The third possibility was another CVAFS instrument: the TEKRAN monitor, which was temporarily available at the laboratory at NILU during September-October 2000. All these instruments were specific Hg detectors with internal radiation sources with λ = 254 nm. The three Hg detectors and some of their properties are listed in Table 3.

Table 3: Hg detectors and some of their properties

Detector	*Analytical method*	*Range*	*Carrier gas*	*Analytical gold trap*	
MERLIN	*CVAFS*	*20 pg-20 ng* *2-2000 ng l^{-1} (solution)*	*Argon*	*External*	*Stationary unit. Available the entire period.*
GARDIS	*CVAAS*	*0.1–1000 pg*	*Oxygen*	*Internal*	*Mobile unit. Available the entire period*
TEKRAN	*CVAFS*	*0.1–2000 ng m^{-3}*	*Argon/Oxygen*	*Internal*	*Stationary unit. Available during September and October year 2000*

4.3.5 Calibration

All three detectors were calibrated by injecting known volumes of saturated Hg gas. The mercury source consisted of Hg° vapour-saturated air in equilibrium with a pool of liquid mercury contained in an enclosed vessel and is illustrated in Figure 8. Desired amounts of mercury were drawn out with a gas tight micro-syringe through a septum at the top of the vessel. The source was kept at room temperature and the exact temperature was recorded on a thermometer, which was in contact with the saturated mercury gas. The actual amount of mercury corresponding to the volumes drawn out may be calculated by formula, but is usually read on ready-made tables (Appendix 1.5). A calibration curve was made by injecting a series of volumes of Hg covering the concentration range expected to be found in the actual

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[2] Refer to Valdal, 2001 for a detailed description of the analytical set-up with the GARDIS detector.

samples. The mercury injections were supplied to the analytical train through an injection port situated in the same position as the TPM-trap in the analytical set-up.

The GARDIS and TEKRAN monitors have injection port units on their front panels.
This gave the opportunity to observe eventual differences between injections made directly on the instrument with injections supplied at other sites in the analytical system.

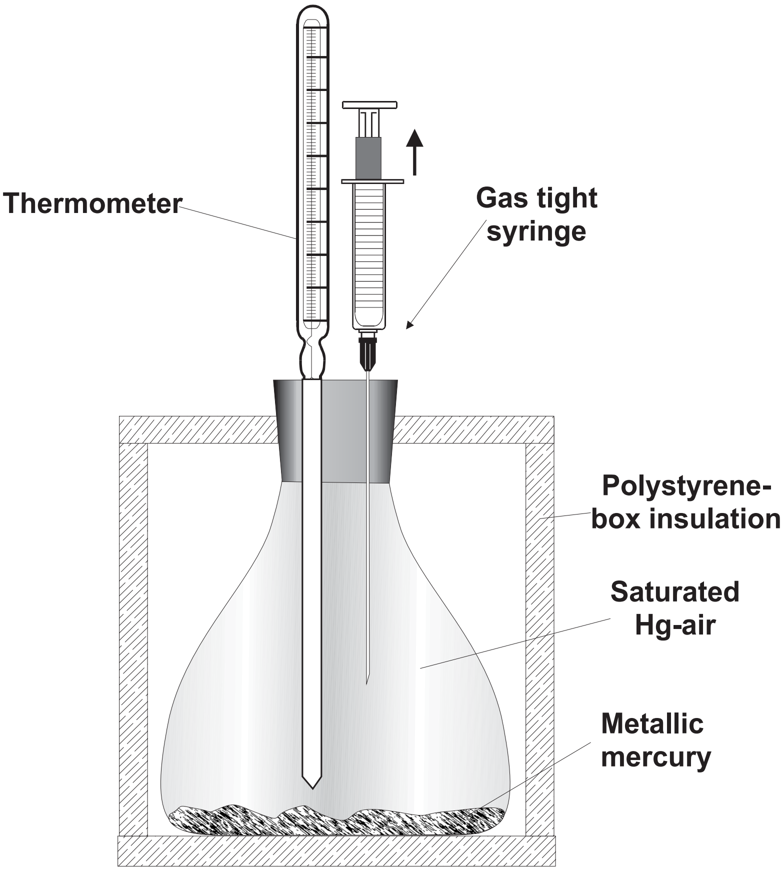

Figure 8: Source of saturated mercury vapour

In the same period as the TEKRAN monitor was available there was also a commercially produced calibration source situated at NILU. This unit had a programmable temperature control and a digital micro syringe for accurate measurement of the volume of mercury gas present.

4.3.6 Tubing, fittings and connections

Primarily teflon was used as tubing material in the analytical set-ups. Viton and silicon tubing served as possible alternatives. In addition bits of viton and silicon, being quite elastic, were used as fittings between the different constituents in the analytical train. For adapting the TPM-trap (outer diameter 13 mm) to the analytical train tubing (outer diameter: 6 or 6.4 mm), a custom made teflon connection was used (see Figure 7). Table 4 lists tubing, fitting and connection materials used in the different analytical systems.

Table 4: Tubing, fittings and connections used in the analytical set-ups

analytical system	*analytical train tubing*	*fittings and connections*	
	Inner/outer **diameter (mm)**	*analytical train - pyrolyzer*	*analytical train – TPM-trap*
MERLIN	*teflon 4.8/6.4* *viton 6/9*	*bit of viton tubing 5/8*	*Custom-made teflon connection fitted to the analytical train with a bit of viton; 6/9, and to the TMP-trap with a bit of viton; 9/13 (see Figure 7)*
GARDIS	*viton 6/9*	*directly*	*Same as for the MERLIN system apart form direct fitting between teflon connection and analytical train*
TEKRAN	*teflon 4.8/6.4*	*bit of viton 6/9*	*Same as for the MERLIN system*

4.4 From sampling to analysis, step by step

Table 5 shows a summary of the procedure for the sampling and determination of particulate mercury when using the TPM-trap.

Table 5: Consecutive steps in the procedure of sampling and determining total particulate mercury (TPM)

A. Preparations	*For cleaning, the different constituents of the TPM-trap were placed in a solution of diluted Br-Cl for 24 hours, after which they were rinsed in ultra clean water in five sequences (see Appendix 1.2 for the preparation of Br-Cl solution).* *The TPM-trap was constructed (using particle free disposable gloves).* *The TPM-trap was further cleaned by coupling it into the analytical train, and heating it for 2 x 12 minutes (or more) at 900 °C, until a stable background signal was observed.* *Both ends of the trap were sealed by custom-made teflon stoppers and packed in double polyethylene bags.*
B. Sampling	*Polyethylene bags and teflon stoppers were removed and the trap was coupled to the end of a sampling line in the sampling box.* *Exact time and the number on the gas meter were registered when sampling was started and ended.* *The TPM-trap was dismantled from the sampling line and the stoppers and the polyethylene bags were added.*
C. Storage	*If the sample (particulate trap) could not be analysed shortly after sampling was ended, it was preserved in a freezer.*
D. Analysis	*The detector and the pyrolyzer along with the carrier gas were switched on one hour in advance for stabilization.* *The analytical trap was heated repeatedly to 450 °C, until a low and constant background signal was observed.* *Manual injections of series of known amounts of Hg saturated gas, produceed a calibration curve.* *The samples were removed from the freezer some time in advance for adjustment to room temperature.* *The particulate trap was put into the analytical line and was heated to 900 °C for 3.5-10 minutes.* *When the TPM oven was switched off, the analytical gold trap started heating to approximately 450 °C. The preconcentrated mercury was desorbed and a signal was observed.* *A manually powered fan was used to cool the TPM-trap/TPM oven. The analytical gold traps had automatic cooling systems in all the three options mentioned (MERLIN, GARDIS and TEKRAN).* *After a given number of samples were analysed, another series of Hg gas injections were made. A regression curve made from the all the injection results constituted the final calibration curve. Evident outliers were excluded.*
E. Data processing	*In the case of using the MERLIN detector, the signal was transferred to an integrator, which transcribed a curve and its area.* *When using the GARDIS, the signal was automatically logged as peak height (software going with the instrument).* *Software going with the TEKRAN automatically integrated peak area of the signal along with statistical data.* *Data for total mercury in the standards as function of peak area/height were noted in a program for regression analysis. The results of the samples were calculated by their peak height or area values and the respective regression curves.*

4.4.1 A separate system for cleaning TPM-traps

At times when the detector unit (GARDIS) was preoccupied, a simplified system for the cleaning of TPM-trap was used. Argon gas was led through a protective gold trap to the TPM-traps which were heated one by one to 900 °C for two times twelve minutes in the custom-made TPM oven. The rear end of the trap was open to ambient air. This was not considered to represent a risk of contamination as the gas flow continually made the internal pressure greater than the surroundings. After the cleaning procedure the trap was placed on a laboratory bench for cooling. A couple of minutes later the trap was clogged with teflon stoppers in both ends and packed in double polyethylene bags. Numerous traps were tested by analysis to confirm that they were satisfactorily clean.

4.5 Conventional method for measuring TPM

shows a summary of the procedure for the sampling and determination of particulate mercury on glass fiber filters. The filters (142 mm in diameter, pore size: 1 μm) are installed in stationary high volume samplers. In the laboratory the filters are wet digested in nitric acid (HNO_3) followed by analysis on the MERLIN detector. This method has been used for measuring particulate mercury during a campaign performed by NILU in 1996-1997 (Berg et al., 2001).

Table 6: The successive steps in the procedure of sampling and determining total particulate mercury (TPM) by the glass fiber filter method

A. Preparations	*Glass fiber filters, 142 mm in diameter (Gelman Type 61635) were cleaned by baking them in a ceramic oven at 450 °C for 24 hours.* *After cooling in a desiccator, each filter was wrapped in aluminium foil and placed in a polyethylene bag.*
B. Sampling	*The filter was unwrapped and placed in a custom-made, permanently installed high volume sampler.* *Air was pulled through the filter by pumps (Siemens ELMO 2BH5) at a flow rate of approximately 5* m^3 h^{-1}*.* *The flow rate was measured by a KHRONE flow meter on a special scale. The numbers were converted to* m^3 h^{-1} *according to a given equation. (Appendix 1.6)* *Time and flow were registered at the start and end of sampling (the sampling flow was calculated as the average of start and stop flow rate).* *When sampling was ended, the filter was folded into a semi-circle with the exposed sides facing each other, wrapped in aluminium foil and put in a polyethylene bag.*
C. Storage	*The exposed filters were stored in a freezer.*
D. Sample handling	*The filters were digested in 20 ml nitric acid* HNO_3 *(1:1) and diluted to 60 ml with ultra pure water (see procedure in Chapter 4.5.1).* *25 ml of the diluted sample was transferred to special sample glasses.* *1 ml of Br-Cl solution was added for further oxidation/conservation. Each glass was capped until analysis was performed.*
E. Analysis	*Hg° gas was generated from the sample by using a vapour generator (PSA 10.003 Vapour Generator) with* $SnCl_2$ *as the reduction agent.* *The Hg° gas was detected by the MERLIN detector.* *Five standard solutions with a concentration range covering the expected results (5, 10, 20, 40 and 100 pg* ml^{-1}*) were run before and after analysis of the actual samples in order to construct a calibration curve. The standard solutions were prepared by an appropriate dilution of a stock solution (Appendix 1.2).* *Sample preparation and analysis were performed in a clean room, class 300.*
F. Data processing	*The detector registered the signal, which was then conducted to a recorder. The height of the curve was measured manually on a transcript.* *Data for total mercury in the standard solutions as function of peak height were recorded in a program for regression analysis. Hg concentrations in the samples were calculated from the peak height values and the regression curve.*

4.5.1 Procedure for acid digestion of glass fiber filters

The glass fiber filters were wet digested according to Norwegian Standard (NS) 4470. The filters were cut into pieces and transferred to 100 ml Duran glasses with teflon coated caps. 20 ml concentrated HNO_3 (suprapure) diluted 1:1 with ultra pure water was added. The glasses were firmly sealed and heated in a pressure boiler at 120 °C for 30 minutes. The samples were cooled to room temperature and then diluted during transfer to clean Duran glasses in several steps to a volume of 60 ml was obtained.

4.6 Field study at Ny-Ålesund, Spitsbergen

A field study for the measurement of particulate mercury was performed at Ny-Ålesund, Spitsbergen during spring 2000.

4.6.1 Setting

Ny-Ålesund, 79.5°N and 11.5°E, has been one of the world's northernmost settlements since the beginning of the twentieth century when a small coal mining community was founded there. During the 1950s the mining activity ceased and completely stopped in 1962 due to a tragic accident. In 1968 the Norwegian government decided to designate Ny-Ålesund as a centre for polar research. Since then an international research community has developed there. A map over Spitsbergen is presented in Figure 9.

Figure 9: Spitsbergen

Ny-Ålesund is situated near the sea-shore on the western coast of Spitsbergen, located on the southern side of Kongsfjorden. Steep mountains, 500-600 m a.s.l., surround the research village. The Norwegian Polar Institute coordinates all research activity and is also owner of the atmospheric research station situated 474 m a.s.l. on the Zeppelin Mountain just outside Ny-Ålesund. The station is located on a mountain ridge, with steep downhills to the north and south and with higher mountain peaks to the west and east. The site is accessible by cable car. The Zeppelin station is a unique location for background measurements of atmospheric compounds, as the influence of ground related contamination is close to non-existing. Further on, all human activity within a radius of 200 meters is forbidden.

The station has been in operation since 1989, and was officially reopened the 2nd of May 2000 after thorough restoration. Compounds such as green house gases, ozone and airborne toxic elements including Hg°, are monitored at the Zeppelin station. In addition, measurements of wind speed, wind direction, temperature, pressure and relative humidity are performed on a continuous basis. (Solberg et al., 1996). The field study for measuring particulate mercury was carried out at this atmospheric research station. During the same period, measurements of gaseous divalent mercury (GDM) were carried out.

4.6.2 Preparations

It was planned to bring an analytical set-up both for the determination of TPM and GDM. The constituents of the analytical train are common for the two species expect the custom designed ovens (TPM-oven and GDM-oven), which are coupled to the system depending on which analysis required. As the only mobile detector unit available, the GARDIS would be brought along. Predominantly the analytical system would be used for GDM because of the necessity of immediate analysis of these samples due to degeneration of the sample material shortly after end of sampling. Wangberg (pers. comm.) stated that TPM samples could be conserved for a couple of months when stored at low temperature. It was evident that the analysis of GDM on denuders followed by cleaning procedures of the denuders, was quite time-consuming (8-10 h per day). Hence, the intention was to bring along a sufficient amount of TPM-traps for sampling a three-weeks' period, store the samples in a freezer, and bring them back to the laboratory at NILU for analysis. However, at times when the analytical train was available, some determinations of TPM could be carried out in the field. Sixty TPM-traps were constructed, cleaned and packed as described in Table 5.

In addition to the sampling of particulate mercury with TPM-traps, the conventional method at NILU for sampling and determining this species would be employed at Ny-Ålesund. Sixty glass fiber filters (142 mm in diameter, Gelman Type 61635) were cleaned and packed as described in Sampling at the Zeppelin Mountain.

The 28th of April the equipment was transported up to the Zeppelin Station. The sampling box was placed on the eastern wall, 1.5 meter above a metal platform.

Sampling was started the 29th of April. Each batch generally consisted of two actively sampling TPM-traps in addition to one blank TPM-trap (some measurements were run without blank). The last samples were made on the 20th of May. Predominantly each batch sampled for 24 hours, except 4 batches, which were run for 48 hours, and 1 batch, which was run for 72 hours.

Field blanks were produced by picking random traps from the sixty pre-cleaned traps. Before a sampling batch was started, the blank trap was unsealed and installed on one of the inlet tubes, taken off again, sealed, and positioned in the wooden box during the period of sampling. The blank traps were stored, transported and treated in the exact same manner as the actual samples.

Before sampling, the traps were additionally pre-cleaned by heating to 900 °C for 12 minutes. The same procedure as described in 4.4.1, was applied. Approximately 50% of the traps were again checked in the GARDIS system to confirm that they were satisfactorily clean.

Two parallels of glass fiber filters collecting particles in custom-made high volume samplers were following a similar time schedule as the TPM-traps (procedure described in Table 6). This TPM sampling method was also employed the rest of the year 2000 at the Zeppelin station, starting at the end of February and continuing after this specific fieldwork was ended till late September. Each sample was collected during five days on a weekly basis and performed by station personnel (only one parallel).

Blanks were obtained by wrapping out random filters, install them in one of the high volume samplers, take them out again and wrap them in aluminium foil (no air flow was actively drawn through the blanks). After sampling the TPM-traps and filters were stored in a freezer. For transportation back to NILU they were preserved in a cooler. The filters were handled as described in Chapter 4.5.

4.6.2.1 Total gaseous mercury and ozone at the Zeppelin Station

During the fieldwork at the Zeppelin Mountain, there was access to continually follow the concentrations of elemental gaseous mercury and tropospheric ozone on monitors permanently situated at the research station. These measurements are maintained by the Department of Chemical Analysis (K-lab) at NILU. The levels of these substances are normally very stable, Hg°: 1-2 ng m^{-3}, O_3: 65-85 µg m^{-3} (Solberg et al., 1996). During the period from late April to the 20th of May, several depletion episodes were observed where the concentrations of Hg° and O_3 were decreasing and sometimes approaching zero. These episodes followed more or less the same pattern, which strongly indicates that these two species are subjected to similar processes leading to their depletion.

4.6.3 Analysis at the Zeppelin Mountain

Preliminary analysis of TPM samples collected on TPM-traps was performed on the GARDIS system located at the Zeppelin station. Standard Hg° injections were made through a calibration port located at the TPM oven. Each TPM-trap was heated to 900 °C for 3.5 minutes. Totally eleven samples were analysed at the Zeppelin station. The rest of the samples were stored in a freezer. For transportation back to Kjeller, the traps were brought in a cooler.

4.7 Field study on the Mediterranean Sea

A field study for the measurement of particulate mercury was performed on the Mediterranean Sea from the 27th of July to the 10th of August, year 2000.

4.7.1 Setting

This field study was the second part of an oceanographic cruise arranged by the Italian Research Council (CNR) taking place from the 14th of July to the 10th of August addressed to investigate air-sea exchange processes of atmospheric pollutants over the Mediterranean Sea. The major focus was on atmospheric and aquatic mercury, but measurements of other pollutants such as NO_x, SO_2 and O_3 were also carried out. Urania was the name of the ship, which was a vessel designed for research activity. It departed from Naples the 27th of July, made a trip around the island of Sardinia, and arrived at the port of Civitavecchia, close to Rome, on the 10th of August. Figure 10 describes the itinerary of the cruise.

Figure 10: Map over the Mediterranean Sea. The red line demonstrates the itinerary for the entire research cruise. The northern semi-circle describes the route between Naples and Civitavecchia

The sampling box was placed on an outdoor railing of metal. The vessel did not present any possibility of a metal-free environment. The pumps were installed outdoor. Each batch consisted of two actively sampling TPM-traps in addition to one blank TPM-trap. Each batch sampled for 24 hours. Shortly before a trap was used for sampling, it was additionally cleaned for 12 minutes at 900 °C and checked on the GARDIS system to confirm that it was satisfactorily uncontaminated.

At night the 4th of August, a violent rainfall made it necessary to discontinue the sampling. The pumps were flooded and needed a complete maintenance the following morning before sampling again could be started. In spite of this wet experience, the two pumps running the TPM sampling lines seemed to work satisfactorily afterwards.

The Italian research group (CNR-Institute for Atmospheric Pollution) at the ship also performed sampling and measurements of TPM by TPM-traps (6 mm in diameter).

4.7.2 Analysis at URANIA

The analytical equipment was installed in the laboratory on the ship's lower deck. Each object had to be properly fastened by ropes in the case of heavy sea. Preliminary analysis of TPM samples collected on TPM-traps was performed on the GARDIS system. Standard Hg° injections were made through a calibration port located at the TPM oven site in the analytical train. Each TPM-trap was heated to 900 °C for 3.5 minutes. Seven samples were analysed on this system. In addition five samples were analysed on the analytical system of the Italian group. The rest of the TPM-traps were stored in a freezer. For transportation back to Kjeller, the traps were brought in a cooler.

4.8 Experiments and analysis with the TEKRAN monitor

The TEKRAN monitor was available from late September to late October at the NILU laboratory.

A traditional set-up for the analysis of TPM was constructed as shown in the schematic presentation in Figure 6. Certain adjustments were made to use the TEKRAN as detector in TPM determination. Zero air carrier gas was led through a protective coal filter (removing humidity) and a gold trap (removing trace concentrations of Hg° in the carrier gas) before it entered the TPM trap and then the pyrolyzer unit on the custom-made denuder oven. The analytical line was coupled to the TEKRAN at the "sample air" inlet at the rear of the instrument. This inlet contained a teflon filter for removing possible particles from the gas stream before it entered the analytical cartridges (particularly important when sampling in ambient air). All the constituents in the analytical set-up were coupled together by teflon tubing. Viton was used as fitting material. The sample rate on the TEKRAN was adjusted to 200 ml min^{-1} ([3]).

For analysis heating-cycles of 5 min of the TPM trap was started simultaneously with a TEKRAN-cycle. When the period ended a fan was activated manually to cool the TPM-trap. The detector automatically continued for another cycle, giving a background value. The system was now regarded as ready for performing analysis of the numerous samples from the field studies at Ny-Ålesund and the Mediterranean Sea. Injections of at least three different volumes of saturated mercury at regular intervals between samples produced a calibration curve. Each sample was generally heated for two 5 min cycles, cooled for 5 min and then heated for another period to make sure that all the mercury present was desorbed during the two first cycles.

4.8.1 Field study at NILU, Kjeller

A field study for the measurement of particulate mercury was performed outside the NILU quarters at Kjeller from the 20th of September to the 13th of October. Kjeller is a suburb situated 20 km northeast of Oslo.

4.8.1.1 Sampling at Kjeller

The sampling box was placed on the wall of a small hut 1.5 m above ground level. The hut was located on a meadow approximately 50 m from the NILU building. At a 100 m's distance in the opposite direction a district road with relatively heavy traffic was passing. Each batch consisted of three or four actively sampling parallels and one blank trap. Two of the parallels were placed in the sampling box. The other two traps were installed in two separate sampling units consisting of a metal pipe poking out 1.5 m perpendicular to the wall ending in protective polyethylene funnels. The TPM traps were coupled to the ends of sampling lines, which were running through the pipes connected to indoor pumps.

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[3] The specifications of the instrument designate a flow rate range of 0.5 – 1.5 l min^{-1}. Conferring with the support personnel at Tekran Inc (D. Schneeberger, pers. comm.) gave the conclusion that the decreased flow rate did not represent a problem.

The samples were analysed as described above. In the same period particulate mercury was sampled on glass fiber filters installed in high volume samplers located in the hut. The filters were handled as described in Chapter 4.5.

4.9 Tests with standard reference material

Tests with adding standard reference material to TPM-traps were performed. Coal fly ash (NIST 1633 b, 0.141 ± 0.019 mg Hg kg^{-1}) was weighed out on a Mettler MT5 microbalance (Greifensee, Switzerland). A small weighing tray was made out of a filter paper. The material, on beforehand well shaken in order to obtain homogenous samples, were added by spatula in the range of 100–8000 µg and the mass was registered. Each sample was transferred quantitatively to a TPM-trap. A stream of compressed air was blown through the trap to ensure that the standard reference material settled on the tiny filter within the trap (the dusty material had a tendency to spread on the walls of the internal tube of the trap). The TPM-trap with the standard reference material was sealed and analysed in the manner described in Chapter 4.4.

4.10 Data handling

A few samples were analysed on the GARDIS system in the field. Each sample was heated for 3.5 minutes. The results, including the standard injections, were corrected for the background (BG) value of the system. Results of samples in picogram Hg were obtained by using the most "sensible" calibration curve acquired during the time of analysis. In a few cases the yield obtained from a sample were lower than the BG of the system. These results were given the value "zero".

When using the TEKRAN system for analysis, each sample was heated for two cycles of five minutes each. The values from the two periods were added and after subtraction of two times the background value of the analytical system, this was treated as the result of the sample. Standard values were equally corrected for the BG of the analytical system.

Results in picogram Hg were obtained by using the calibration regression curve based on standard injections made through a calibration port positioned at the similar site as the sample (TPM-trap) in the analytical train.

All sample data were corrected for the average field blank value obtained from the respective fieldworks. In cases were the field blank value exceeded the sample value, the sample result was set to zero.

Data processing, regression analysis and correlation analysis were performed in Microsoft Excel (office 2000).

5 Experiences made along the way

5.1 Preliminary experiments

5.1.1 Experiments with the two-oven system and the MERLIN detector

To begin with, a preliminary system was put up with the existing two-oven system (used for conventional Hg° analysis). Oven 1 contained the pyrolyzer and oven 2 contained the analytical gold trap. The MERLIN was the detector unit at the end of the analytical line. The whole set-up was permanently installed at the clean room laboratory at NILU. During late March to late April year 2000, substantial effort was put into making this analytical train operate satisfactorily. Predominantly, that entailed achieving a low and stable background signal in addition to attaining an acceptable calibration curve.

The system was normally used for determination of total gaseous mercury with samples giving a signal corresponding to approximately 0.8 ng. In comparison, a 24 hour sample of TPM (with an air volume of ~5 m^3) would normally give a signal of approximately 0.025 ng. Thus, TPM determination would be much more sensitive for interferences. It turned out quite challenging to obtain a low and stable background signal.

The general approach was to start out with a minimal analytical train, clean it (by flushing argon gas and repeated periods of heating) and then introduce a new constituent one by one until a complete set-up for TPM analysis was accomplished. To begin with a system consisting of the analytical gold trap (oven 2) and the detector was tested. The different constituents were coupled together by fittings and tubing made of viton, teflon and silicon. Different analytical gold traps were tested and judged adequate according to their cleanness and the shape of the curve they displayed (symmetry, tailing etc.). The analytical gold trap was heated repeatedly to 450 °C until a constant background signal was achieved. The next step was to introduce the pyrolyzer. Julia Lu (pers. comm.) recommended a pyrolyzer temperature of 900 °C. Oven 1 was set to 900 °C and the pyrolyzer was heated for 10 minutes at this temperature for cleaning before it was coupled to the remaining analytical train. Still, a considerable signal/contamination was released from the pyrolyzer when activated. The inert quartz material constituting the pyrolyzer should in theory give no contribution of contamination whatsoever. After numerous periods of heating, starting with the pyrolyzer for 5 minutes followed by the gold trap for 1 minute, there were still extensive noise signals registered. Particularly disturbing was the fact that a substantial signal occurred during the warming up of the pyrolyzer. This signal increased steadily during the 5 minutes of heating, exceeding the range of the detector, and ceasing only when the oven was turned off and cooled. Any mercury vapour present should be collected on the gold trap and released in one discharge, only when the analytical trap was heated. A possible reason for this undesirable signal could be that the amount of mercury exceeded the amalgamation capacity of the gold trap, however, this seemed unlikely since the amount of gold present in the trap should be abundant for absorbing the Hg sample in question. Furthermore it seemed highly improbable that any constituent in the system could contain mercury at the registered level. Another theory was that the heating of oven 1 to 900 °C influenced/increased the temperature of oven 2, positioned only approximately 10 cm away, and thereby making the gold trap emit Hg° before this oven was energized. Yet, measurements made it clear that the two ovens did not influence each other’s temperatures to an extent that would make this a possibility.

A temperature check of the two-oven system made it evident that the internal temperature sensor showed readings which were substantially lower than the actual temperature (measured by a multimeter). For instance when oven 1 was adjusted to 600 °C, the multimeter reading showed 950 °C, after heating for 2 minutes. This difference was probably due to the internal sensor being old and worn. Hence, after some additional measurements it was found that oven 1 had to be adjusted to 500 °C to obtain a true temperature of 900 °C and oven 2 had to be adjusted to 400 °C to obtain 500 °C. Regular checks of the oven-temperatures were performed in order to approach controllable analysis conditions. After these adjustments were made, no signal during the heating of oven 1 was registered.

The electronics of the two ovens were interrelated. Oven 1 had to be switched off (end a period of heating) before oven 2 could start energizing the analytical trap. Thus, constant heating of the pyrolyzer was impossible with this system. In theory it should not be a problem that the pyrolyzer was activated temporarily, since the periods of heating could easily be adjusted to the adequate time for the sample to pass through. However, it turned out that each time a new period of heating started some contamination related to the pyrolyzer was released. This might be due to impurities collected in twists and turns in the tubing, which were released when heated gas was flowing through the pyrolyzer during the heating. Otherwise it could be generated from an unforeseen source. The tubing and fittings close to the hot area could perhaps emit interfering substances as a result of the violent heating (although quartz is a heat resistant material, heat will to some extent be radiated to the surroundings). Anyhow, this impaired the background signal and made the analysis less sensitive. It seemed more advantageous to have a system with continuous heating of the pyrolyzer. This could be obtained by using the pyrolyzer unit on the custom-made GDM oven.

At the time being it seemed relatively difficult to obtain a reliable stable system with the two-oven system and the MELRIN detector. Time was running out before a planned departure to Ny-Ålesund, Spitsbergen. It was judged more advantageous to use the remaining time to attempt achieving a functioning system with the pyrolyzer unit on the custom-made GDM oven and the GARDIS detector.

5.1.2 Experiments with the GARDIS detector

Since the GARDIS was the detector unit that would be brought along to the Ny-Ålesund field study, attention was addressed to make an analytical train for the determination of TPM with the GARDIS as detector unit. A system was put up with the pyrolyzer unit on the custom-made denuder oven. The quartz tube containing broken bits of quartz could now be kept at a constant temperature of 900 °C.

To begin with calibration was performed on the GARDIS as the only constituent in the set-up. The background values were low, but repeated injections of identical volumes with saturated mercury gave poor precision and accuracy. After some time of testing, the "chopper speed[4]" on the detector was adjusted, leading to a considerable improvement of both accuracy and precision.

When the pyrolyzer was included in the system, new problems arose. The background level increased significantly, but injections of known amounts of Hg° gave reduced outcome. The calibration constant on the detector was adjusted but the results of the injections did not

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[4] Refer to Valdal, 2001 for description of "chopper speed".

increase correspondingly. After each constituent in the set-up was by-passed, it was evident that the pyrolyzer was the source of the problem. Ingvar Wangberg at the Swedish Environmental Research Institute (IVL) in Göteborg, had experienced similar problems with old and worn quartz, which seemed as if it absorbed the injected mercury. However, these episodes arose only when the quartz material was cold. In the present case the quartz was kept at 900 °C. To exclude the possibility that the decreased outcome of Hg° injections was caused by impurities in the quartz, the pyrolyzer was put in a solution of Br-Cl in 48 hours. After the cleaning procedure, injections were first run through an empty quartz tube, which gave slightly improved results. The quartz tube filled with quartz bits still gave low yields. In addition it was registered that the first couple of injections generally gave severely poorer results than the consecutive ones. After further correspondence with Wangberg, it was decided to exclude the pyrolyzer from the analytical train during the rapidly approaching field study at Ny-Ålesund. The organic components which the pyrolyzer was predominantly meant to remove would presumably be present in negligible concentrations in the Arctic atmosphere.

Tedious work with cleaning denuders for GDM sampling occupied the GARDIS system for long time periods. A separate system for cleaning TPM-traps was erected temporarily. The work with preparing sixty samplers was time-consuming and at that moment quite pressing. Numerous traps were cleaned according to the “simplified” procedure described in chapter 4.4.1.

5.2 Mediterranean Sea

5.2.1 Preparations for the Mediterranean Sea research cruise

Since the GARDIS was the detector unit that would be brought along at the Mediterranean Sea research cruise, continuous efforts were made to improve this system. This work was utterly important because of shortage of available TPM-traps, which made it necessary to be able to perform analysis at the research vessel. When the equipment arrived from Spitsbergen it was erected at the laboratory at NILU. It soon became evident that there was a leakage inside the monitor. The work with trying to locate this leakage proved unsuccessful and an additional problem arose, as the optical absorption cell was broken. It was decided to send the monitor to the manufacturer in Lithuania. After the reparation, there was still a leakage in the system. After some time’s investigation it was located in the analytical train in a filter holder containing a dust filter positioned down-streams of the GARDIS. After replacement with a new and tight holder, a low and stable background level was obtained.

The pyrolyzer would be needed, as the level of organic components might be at an interfering level in the Mediterranean area. Bearing Wangberg’s advice in mind, new quartz was broken and filled into a new quartz tube. In advance the material was cleaned for several days in a solution of Br-Cl (Appendix 1.2) and rinsed in ultra clean water in five sequences. A considerable improvement was registered. As opposed to earlier, standard injections now gave similar results with and without the pyrolyzer. It was concluded that the earlier problems were due to “contaminated” quartz constituting the “old” pyrolyzer.

5.2.2 Analysing at URANIA

The analytical equipment was installed in the laboratory on the ship's lower deck. Each object had to be properly fastened by ropes in the case of heavy sea. When the installation was completed, the GARDIS was started. In the beginning the background level was both elevated and unstable. After 24 hours with running background measurements, it was registered that the values were dependant upon room temperature in addition to the degree of activity in the laboratory. The air conditioning did not work very well so the doors were usually left open, leading to a varying room temperature. Eventually, the background level was sufficiently stabilized so that only diurnal variations were seen.

Calibration was initiated using a room-temperature mercury source. The yields of subsequent injections of similar amounts of Hg° were varying substantially. The needles of the syringes were substituted by new ones, and injections with several different microsyringes were performed. None of these operations pinpointed the problem. The calibration constant of the instrument was adjusted several times. Frequently worn-out tubing ends were cut off to prevent leakage in the system and the loosening of small particles from the tubing material into the analytical line. Measurements of ambient air Hg° in the laboratory gave a result of 10-20 ng m^{-3} mercury. This is quite elevated compared to normal indoor values of approximately 3-10 ng m^{-3}.

For the GDM samples there was no choice. Fast degradation of the sample material made it compulsory to use the system with or without an appropriate calibration curve. A few attempts to analyse TPM samples were made. The results did not exceed the detection limit of the system (except for one sample). The actual samples and the blind traps had similar results. It seemed as if the mercury in the samples "disappeared". The Italian group also got strange results, but at least they registered an outcome. The Italians had a similar analytical set-up, with a TEKRAN model 2500 as the detector and argon as the carrier gas. It was agreed to run the Norwegian TPM-traps on the Italian system for comparison. A few adjustments with fittings were made to install the Norwegian TPM oven into the Italian system. Analysis of a few samples at the Italian system gave results around 20 pg m^{-3}. The parallels were similar and the blank values were relatively low. Eventually this system rendered difficult to operate as well. It did not seem possible to obtain an acceptable calibration curve. At this time there were a sufficient number of traps available to sample the rest of the period. It was decided to store the rest of the samples in a freezer at hand in the laboratory and analyse them at NILU. For transportation the traps were brought in a cooler.

For the GDM determination on the GARDIS system no outcome was registered as long as the pyrolyzer was present in the set-up. After exclusion of this unit, results within the expected range were obtained. However, it was not possible to obtain a calibration curve to evaluate the results.

During the entire stay at the Mediterranean Sea, the analytical system was quite unstable. Most often the background level was elevated and standard injections gave highly varying results. Several attempts of trying to locate the problem rendered unsuccessful. The other research groups present at the ship also experienced severe problems with their systems. Especially the calibration of the instruments was troublesome. The constant movements of the ship may be part of the explanation to these complications. In addition, inconsistent electricity supply, contamination of the laboratory area and great temperature variations could have negative effect.

5.3 Experiments and analysis with the TEKRAN monitor

Initially the TEKRAN was set to operate without the rest of the analytical train. Calibration was started, first automatically and then by manual injections. The injected volumes, however, had yields of only 60% of the true values. After some scrutiny it was revealed that the instrument had been calibrated without zero air coupled to the right inlet port. The mistake was corrected and new autocalibration was initiated. It was now registered that the background level was too high. Different tests were carried out to detect a possible leakage in the system. No leakage was revealed, but still the background remained elevated. Then the suspicion went to the septum in the calibration port on the front of the instrument. It was replaced by a new septum and the values improved considerably. After an additional automatic calibration, manual injections were performed. Now there was perfect agreement between the added amount of mercury and the result produced by the TEKRAN.

The instrument was set to run 5 min cycles of sampling. The background levels rose. Replacing the teflon tubing between the pyrolyzer and the detector had a positive effect and a background value of approximately 1 pg l^{-1} was established. At this point manual injections of saturated mercury gas were supplied alternately through the TEKRAN injection port and through an injection port located at the TPM-oven site in the analytical line. There was a deviation between the two measurements; the injections through the TPM injection port being generally 10 – 20% lower than the direct injections. Considerable effort was made to locate the cause of this deviation. Each constituent in the analytical set-up was by-passed, the pyrolyzer was repeatedly cleaned in Br-Cl solution, the calibration port was tested at different locations in the analytical train, and the teflon filter in the “sample air unit” was changed. Though, the results remained the same. Eventually, it was decided to base the calibration curve on the results from injections on the TPM injection port. These measures represented the most similar situation compared to the actual samples.

6 Evaluation of the method

6.1 Introduction

The main focus has been devoted to evaluating the sampling and determination of total particulate mercury by the TPM-trap method, as this was the main task of this thesis. However, work was also done in order to settle a satisfactory procedure for the sample handling of glass fiber filters. Hence evaluation of the sample handling and analytical procedure of glass fiber filters is included. The sampling of TPM on the glass fiber filter is not treated in this section.

6.2 The TPM-trap – considerations of which model to choose

Lu (1998) developed this sampler during the mid-nineties. The initial model contained a thread-connection to keep the inner and outer tube satisfactorily together. A couple of years later, Wangberg at the Swedish Environmental Research Institute (IVL) simplified the trap by using a piece of silicon tubing to hold the two quartz tubes together instead of the thread-connection. The silicon-connection was advantageous for two reasons: Silicon tubing is much cheaper than making thread-connections on each trap. Further silicon allegedly exerts an increased pressure on the tube junction. By extending the silicon rubber just prior to putting it in place, the inner tube will be pushed towards the junction as the rubber is contracting. It takes a very accurate glass blower to obtain a similar effect of the thread-connection. The silicon somehow sticks to the quartz and thereby makes the connection completely tight. This is a necessity and also demands thoroughly precise work of a glass blower in the case of using the thread solution.

Due to the fact that the number of traps needed to perform a field study of one month's duration in the Arctic, would amount to approximately 60 traps, the Swedish (cheapest) version was chosen. However, there were certain drawbacks with the Wangberg model as well. The "reaction" between silicon and quartz keeps the connection tight, but at the same time it performs heavy stress on the quartz, which is a rather fragile material. Thus a substantial number of the traps were broken in the connection area after some time's usage. Further more, the Swedish model was far more difficult to construct. To get a satisfactorily tight connection, the silicon rubber had to "embrace" both the inner and outer quartz tubes. Silicon tubing with inner/outer diameter of 9/13 mm was evaluated to be satisfactorily firm. This, however, appeared to be a challenge to put together. An expansion tong made the construction of the TPM-trap a lot easier.

The initial models of the trap fitted a quartz filter with 6 mm in diameter. At the time being this was the only size tested both in Canada and Sweden. Due to the extremely low levels of Hg_{part} in the polar atmosphere (1-5 pg m^{-3}) (Lu et al., 1998; Berg et al., 2001), it would be necessary to sample a minimum of approximately 5-7 cubic meters of air in this area, in order to obtain a detectable signal. This could either be achieved by sampling for sufficient periods of time, or by increasing the diameter on the traps so that a higher flow rate of air could be pulled through. In order to measure and distinguish potential episodes of elevated levels of Hg_{part} in the Arctic, it was of great interest to sample with as high temporal resolution as possible. Thus, it was decided to make a trap which fitted a filter of 10 mm in diameter in order to obtain improved temporal resolution of the measurements.

6.3 Risk of contamination

Sampling and determination of a species normally present in a concentration of only a few picograms per cubic meter air, are evidently extremely susceptible to contamination. Great attention must be devoted to minimize the risk of introducing "pollution" at every step in the procedure.

The TPM-traps and glass fiber filters were cleaned according to the procedure described in Chapters 4.4 and 4.5. During all sample handling involving traps/filters, clean or with samples, particle free disposable gloves were used.

Gaseous mercury was present in the laboratory ambient air at approximately 3 ng m^{-3}. Great concern was taken to minimize the risk of contamination by consequently keeping traps and filters (clean and with sample) stopped and packed.

Using blanks at different levels (analytical instrument, sample handling) works as a control of contamination introduced during laboratory work. Field blanks are a measure of contamination contributed during the additional sample handling steps the method is subjected to during fieldwork. The field blank levels were significantly higher than the laboratory blanks. This is coherent with the assumption that the probability of contamination and error is assumed to be greater during fieldwork compared to sample handling and analysis performed in the laboratory. This is based on the existence of routines normally developed and elaborated in the laboratory in order to limit and quantify errors.

6.3.1 Field blanks

6.3.1.1 TPM-trap

The blanks were randomly picked from the sixty pre-cleaned traps. Before a sampling batch was started, the blank trap was unsealed and installed on one of the inlet tubes, taken off again, sealed, and positioned in the wooden box during the period of sampling. This procedure was carried out to reveal any possible contamination from the sampling system. The blank traps were stored, transported and treated in the exact same manner as the actual samples.

6.3.1.2 Glass fiber filter

Blanks were obtained by occasionally wrapping out random filters, install them in one of the high volume samplers, take them out again and wrap them in aluminium foil (no air was actively drawn through the blanks). After sampling the filters (and TPM-traps) were stored in a freezer. For transportation back to NILU they were preserved in a cooler. The filters were handled as described in Chapter 4.5.

Three field blanks obtained at Ny-Ålesund during the period February – April and June – September 2000 by station personnel, were not going through the procedure with unwrapping and installation in the high volume sampler and are hence considered to be transport blanks only.

6.4 Sampling with TPM-traps

6.4.1 The sampling box

The sampling box was made of plywood because this is a material believed to contribute very little contamination as far as the species of interest are concerned. The box contained a small oven to keep the temperature within the box at approximately 10 °C. This was necessary for successful sampling of GDM and was installed to avoid condensation of water droplets in the denuders. For the sampling of TPM on the contrary, it was advantageous to keep it as cold as possible, as increased temperature could lead to evaporation of Hg° associated with particles. Anyhow the oven did not represent a problem, as the actual filter collecting the particulate material was situated at the exterior of the very box.

6.4.1.1 Position of the sampling box

Certain criteria should be fulfilled when positioning the sampling box:

1. The box should be placed at least two meters above ground level in order to avoid possible influence of emissions of mercury form the soil.
2. There should be minimal human activity in the surroundings of the sampling box. Human activity is considered as a source of possible contamination.
3. The box should be placed at a safe distance from material (e.g. metals) possibly containing small amounts of mercury.

It turned out to be difficult to satisfy these criteria. The box had to be reasonably available for changing samples and the necessity of keeping the pumps indoor required a compromise when it came to the positioning of the sampling box.

At Ny-Ålesund the box was placed on the eastern wall 1.5 m over a metal platform and thereby violating criterion 1 and 3. Apart from the undersigned and a fellow student, only one additional person (station engineer) was passing the sampling box (once every 24 hours). Human activity within a radius of 200 meters of the station was forbidden. Hence criterion 2 was fulfilled.

At the field study on the Mediterranean Sea the box was put on a metal railing (1.5 m above the deck). The boat did not present any possibility of a metal-free environment. There was moderate human activity in the area around the box as it was positioned close to the entrance of the bridge. Hence all three criteria were more or less violated.

At Kjeller the sampling box was placed on the wall of a small hut 1.5 m above ground level. Again easy access to the box in addition to the necessity of keeping the pumps indoor made an optimal positioning of the box difficult. Criterion 1 was violated.

Improved sampling conditions could be obtained by fastening the box on a pole with a system for hoisting and lowering the box. In this case, sampling could be performed several meters above ground level. Longer electrical wires and longer sampling lines would make it possible to position the pole with the sampling box at a distance from possible contaminants (metal material, painted walls, human activity etc.).

The main purpose of the sampling box is the possibility of installing traps outdoor, hence, air may be sampled directly through the TPM-trap without passing inlet tubing. Such inlet tubing, a necessity if the TPM-traps were to be kept in-door, represents a potential negative effect on the air sample before it reaches the filter within the trap. In cases where inlet tubing cannot be avoided it should be kept as short as possible and the preferred tubing material is teflon. This material represents the minimal risk of interferences on the air sample, compared to glass and stainless steel (Lu and Schroeder, 1999).

6.4.2 Gas meters

The gas meters were calibrated at I-Lab twice during year 2000. The total amount of air was calculated by multiplying with a certain calibration constant specific for each gas meter (Appendix 2.1).

6.4.3 Pumps

The pumps could pull a maximum flow of 7 l min^{-1}. It was desirable to sample as large a volume of air as possible on a shortest possible period, hence, no restrictions were used for regulating the flow. The trap itself served as the sole resistance to the airflow. The small individual differences between the traps and the various amounts of material sampled on the filter from time to time influenced the flow to alter accordingly. The registered flow was usually in the range of 3-6 l min^{-1} in the different field works (Appendix 3.1-3.3).

6.4.3.1 Adequate flow rate during sampling

An experiment with two traps sampling in series was performed in order to check whether all the particulate material was retained on the first TPM-trap or if breakthrough occurred, resulting in a signal on the second trap as well. Analysis showed that particulate mercury was primarily collected on the first trap as the second trap in the series gave a signal constituting 15 - 20% of the first one. It was assumed that the applied flow rate of 5-6 l min^{-1} gave satisfactory sampling conditions. However the data are too few to draw any firm conclusions. In addition the analysis was performed on the GARDIS (judged not to be reliable), the pyrolyzer was excluded and the data were not corrected for field blank values. All this adds further “weakness” to the assumptions made. Hence more extensive testing should be performed in order to evaluate thoroughly the issue of sampling flow rate.

6.4.4 Leakage

During sampling it is imperative to be alert to detect possible leakages. Holes in the sampling line would contribute error to the results, because the gas meter would register air not sampled through the filter.

6.4.5 Storage of TPM samples

As a general rule it is advantageous to analyse a sample as soon as possible after sampling is ended. By doing so, several possible interferences are eluded. Is the sample stable? Are the samples exposed to contamination during transport and storage? These are questions not necessary to consider in the case where immediate analysis is performed. However, particulate mercury samples are assumed to be stable when stored at a low temperature. According to Wangberg (pers. comm.), TPM samples can be conserved for a couple of months without adding interferences. Still it would be recommended to make a test as to what extent long storing periods influence the results. Due to time restrictions it was not feasible to perform such testing during the work with this thesis.

6.5 The analytical train

6.5.1 TPM oven

Substantial effort was rendered to make a complete construction with all the constituents: a heating coil, a voltage source (transformer), a time regulation in addition to fittings for the trap and a fan for cooling, installed in one box unit. This proved, however, to be a somewhat difficult task. It was troublesome to find insulation material that could protect the surrounding objects from the strong heat radiating from the heating wire. Several options were tested, but finally it was decided to take into use a preliminary model of the oven. The heating ribbon was erected externally of the box on a plate of steel, connected with the transformer by electrical cables, as described in Figure 7 (Chapter 4).

The heater ought to be further developed. Frequently taking TPM-traps in and out of the system inflicts constant strain on the relatively elastic heating ribbon and its electrical connections. This again impairs the effect and temperature of the heating wire and may lead to varying experimental conditions between the analyses. A more stable system can be obtained by putting a quartz tube between the TPM-trap and the heating ribbon.

6.5.2 Tubing

In the work with constructing an analytical set-up for the determination of particulate mercury, strong attention has to be devoted to the risk of contamination. Information from experienced scientists (I. Wangberg; J. Lu; N. Pirrone, pers. comm.) stated that the tubing material appropriate for this kind of analysis was primarily teflon. In addition viton and silicon tubing could serve as fitting material.

Attention was addressed to make the distance between the protective gold trap, the TPM oven, the pyrolyzer and the detector as short as possible. Unnecessary length of tubing and twists and turns of the analytical line was regarded as disadvantageous.

6.5.3 Calibration curve

Standard injections were made before and after series of sample analysis to correct for any drift in the detector. Normally five levels of the standard constituted the calibration curve, covering the expected range to be found in the samples. The calibration curve was produced by plotting the injected amount of Hg (X) against the instrument response (Y). The correlation coefficient (R^2) between X and Y was determined by least square regression.
When $R^2 > 0.985$ there was satisfactory linearity between the two values in the given range (Tønseth and Døhl, 1996). This criterion was met during all the analyses performed with both methods: TPM-trap and glass fiber filter method.

Saturated Hg vapour and standard Hg solutions are pure samples of the analyte and may not reflect the composition of the actual sample, which in some cases may contain interfering impurities affecting the signal. This will lead to error as the sample results are calculated against the calibration curve.

6.5.4 Analysis of TPM samples on the GARDIS system

The analytical set-up with the GARDIS as detector unit was used for a few TPM determinations during the fieldworks at Ny-Ålesund and the Mediterranean Sea. This system however was never found to be reliable. This was mostly due to the consistent problems with obtaining an accurate and reproducible calibration curve. Nevertheless the data obtained by this method are presented in the result chapter. It is noted in the raw data (Appendix 3.1 and 3.2) which results were obtained by which method. No further evaluation of the GARDIS system will be given in this work[5].

Further on (Chapters 6.6-9) the term “TPM-trap method” denotes the sampling of TPM on TPM-traps followed by determination on the analytical set-up with the TEKRAN detector.

6.6 Detection limits

The detection limit (DL) is defined as the lowest amount or concentration of analyte which can be detected with an acceptable statistical significance (Tønseth and Døhl, 1996). The detection limit is given by equation 12:

$$DL = 2 \cdot t_{0.95} \cdot SD_b \tag{12}$$

$t_{0.95}$ = Student’s t-factor at 95% confidence interval. The t value is dependent on the number of measurements

SD_b = Standard deviation of blank samples

The limit of detection may be defined on different levels. Level 1 and 2 in the paragraphs below represents detection limits based on blank values obtained from the analytical (instrumental) procedures and sample handling in the laboratory. Level 3, based on the field blank values, is the detection limit employed for the entire method. For sample results below the level 3 detection limit, it cannot be discerned whether the signal is a result of an actual sample or simply the effect of contamination. This DL is significantly higher than those based on blank values of different steps in the analytical procedure.

6.6.1 TPM-trap method

The detection limit for the TPM-trap method was calculated on the basis of blank values obtained at three different levels:

Level 1: Blank signal when a clean TPM-trap is cold
Level 2: Blank signal when a clean trap is heated
Level 3: Field blank TPM-traps

The DLs obtained are listed in Table 7 (raw data: Appendix 2.2, Table A).

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[5] Refer to Valdal, 2001 for a detailed description of the GARDIS system.

Table 7: Detection limits for the TPM-trap method

	TPM-trap method	
	pg	*pg m^{-3} (24 h)^{a}*
Level 1 (N=10)	*0.5*	*0.1*
Level 2 (N=10)	*1.5*	*0.3*
Level 3 (N=10)	*14.9*	*2.5*

6.6.2 Glass fiber filter method

Likewise the detection limit for the glass fiber filter method was calculated on the basis of blank values obtained from the following three levels:

Level 1: Signal obtained from blank solutions
Level 2: Signal obtained from blank filters
Level 3: Signal obtained from field blank filters

The DLs obtained are listed in Table 8 (raw data: Appendix 2.2, Table B).

Table 8: Detection limits for the glass fiber filter method

	Glass fiber filter method		
	pg	*pg m^{-3} (24 h)^{a}*	*pg m^{-3} (5 days)^{b}*
Level 1 (N=13)	*141.9*	*1.0*	*0.2*
Level 2 (N=6)	*240.9*	*1.7*	*0.3*
Level 3 (N=8)	*1335.5*	*9.5*	*1.8*

[a] Equivalent values for 24 hour samples at a typical flow rate of 4 l min^{-1} (TPM-trap method) and at a flow rate of 100 l min^{-1} (Glass fiber filter method).
[b] Equivalent values for 5 days' samples at a typical flow rate of 100 l min^{-1} (glass fiber filter method)

The level 3 detection limits are quite high, especially for the glass fiber filter method, something which is an expression of the elevated uncertainty introduced in the field. The DL for 24-hour samples is 9.5 pg m^{-3} (glass fiber filter method), a value which exceeds the background level of particulate mercury of only a few picograms per cubic meter air. A combination of relatively high field blank values and low sensitivity of the method is a reasonable explanation of this high-level limit of detection of the glass fiber filter method.

Results of the samples beneath the detection limit (level 3) are nonetheless included in tables and figures (the results in question are marked by "*" in the raw data section (Appendix 3.1 – 3.3).

6.7 Accuracy and precision

Precision is the closeness of agreement (degree of scatter) between a series of measurements obtained from multiple sampling of the same homogenous sample under prescribed conditions. Precision may be performed on three levels: repeatability, intermediate precision and reproducibility. Repeatability is expressed by the variation of successive measurements obtained by the same method under similar conditions. Intermediate precision is the closeness of agreement (degree of scatter) between repeated measurements made within a laboratory under different conditions, e.g. different days and temperature. Reproducibility expresses the precision between laboratories (Tønseth and Døhl, 1996). In this work, when obtaining relative standard deviations less than 5% for replicate standard samples, the precision was judged to be satisfactory.

Determination of particulate mercury sampled on TPM-traps by dry pyrolysis and CVAFS (and CVAAS) is a destructive analytical procedure, hence, the possibility of running replicate samples was not present. Concerning the glass fiber filter method; the minimal amount of sample present on the glass fiber filters excluded the possibility of parallel digestion of samples. Hence, when evaluating the precision of the analytical procedure, standards (Hg vapour injections, standard Hg solutions and standard reference material) were applied.

Accuracy is the closeness of the measured analyte value to the true value. One procedure to estimate the accuracy of a method is by analysing a standard reference material containing known quantities of the analyte. When accuracy is estimated by analyte recoveries, it can be calculated as shown in equation 13.

$$accuracy\ as\ recovery\ (\%) = \frac{measured\ amount}{added\ amount} \cdot 100\% \tag{13}$$

6.7.1 Hg determination with the TEKRAN system – test of accuracy and intermediate precision

The accuracy and intermediate precision of the analytical set-up for TPM determination with the TEKRAN as detector, was assessed by injections of saturated Hg vapour through a calibration port situated at the same site as the TPM-trap in the analytical train. Using the same procedure for evaluating the accuracy as for calibration is possible since the TEKRAN is automatically calibrated by an internal calibration source and hence not only gives a response in area but also calculates a "true" value of Hg. The test for accuracy and intermediate precision was based on six series of Hg° injections made on three different days. The results are listed in Table 9 (raw data: Appendix 2.3, Table A).

Table 9: Parameters for the determination of accuracy and intermediate precision for Hg analysis performed on the analytical set-up with the TEKRAN

Theoretical value (pg)	*28*	*56*	*111*	*278*	*557*
Reported value (pg)	*25.1*	*48.8*	*96.6*	*237.2*	*475.2*
Number of parallels, N	*6*	*6*	*4*	*6*	*6*
SD (pg)	*0.7*	*1.9*	*1.1*	*4.8*	*12.6*
RSD (%)	*2.7*	*4.0*	*1.1*	*2.0*	*2.7*
Confidence interval at 95%	*24.5 – 25.6*	*47.19 – 50.37*	*95.05 – 97.60*	*233.24 – 241.12*	*464.80 – 485.54*
Accuracy as recovery (%)	*90.0*	*87.6*	*86.5*	*85.2*	*85.3*

The recovery values ranged from 85 to 90% (decreasing slightly with increasing amounts of mercury), indicating a systematically low yield (error). A possible explanation may be that some of the mercury was "lost" out of the analytical train before it reached the detector. The alternative that the reduced yields was due to an internal error of the instrument was ruled out by the fact that Hg° injections made directly through the front panel calibration port on the instrument, gave fine outcomes. It is assumed that an equivalent loss was experienced during sample analysis, hence, the TPM results were obtained by using the calibration curve made by injections in the analytical train.

All the RSD values were below 5%, which indicates that the intermediate precision was satisfactory.

6.7.2 TPM-trap method – accuracy and precision

The accuracy and precision of the TPM-trap as a sampling method was assessed by adding known amounts of standard reference material to TPM-traps followed by analysis on the analytical set-up with the TEKRAN. Altogether 69 repetitions were made using a random selection of 22 TPM-traps. The results were far from satisfactory as the recovery-values were varying extensively within the range: 13 - 102%. When organizing the yields made by each individual trap consecutively, a pattern appeared. As depicted in Figure 11 some traps consequently gave high yields whereas others gave rather poor results (raw data: Appendix 2.3, Table C).

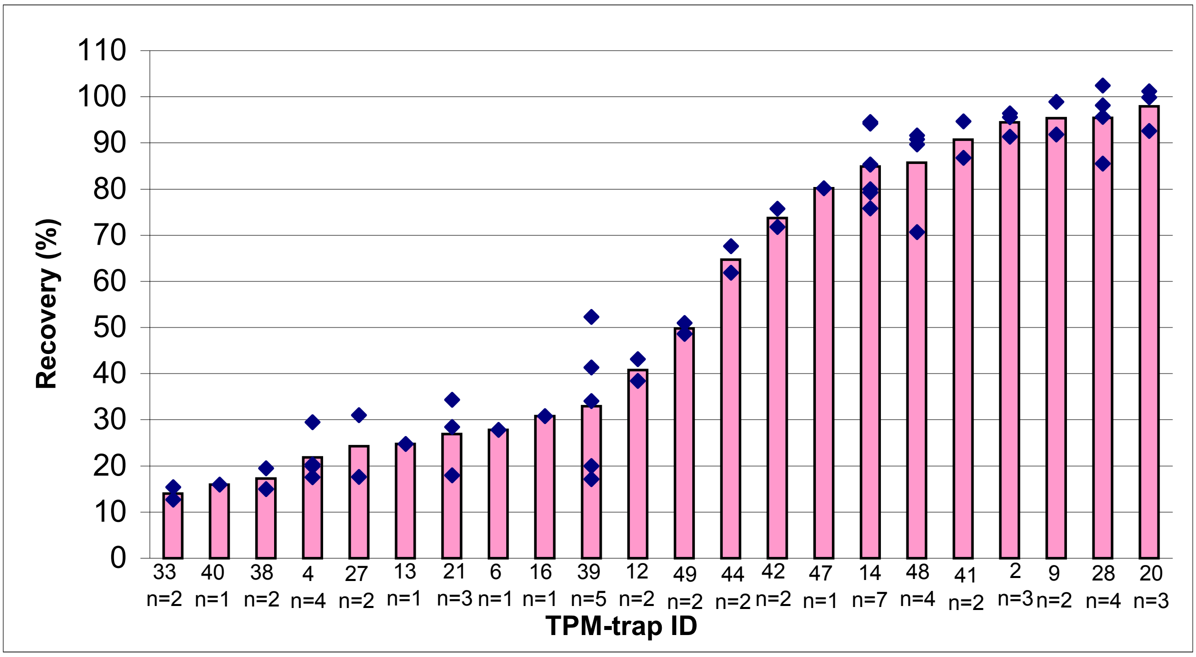

Figure 11: Recovery values of standard reference material applied on TPM-traps. Each column describes the average value for each trap, the dots indicate individual measurements, n is the number of repetitions made with each trap

TPM-trap 2, 9, 20 and 28 gave recoveries between 90 and 100%, an accuracy which is acceptable. TPM-trap 33, 38 and 40, however, produced recoveries between 10 - 20%. The individual dots display the reproducibility for each trap, and the scatter generally lay within an interval of ± 20% of the average (except trap 4, 21, 27 and 39 which had greater scatters).

A test was performed in order to sort out whether the specific recovery values linked to each trap stayed the same also after the trap was dismantled, cleaned and repacked. The results indicated that the recoveries changed significantly when a trap was going through this procedure. TPM 2 originally gave a high yield of 94%, after dismantling, cleaning and repacking the yield was reduced to 21%. Figure 12 illustrates the change in recovery after repacking for TPM 2 and TPM 6 (raw data: Appendix 2.3, Table D).

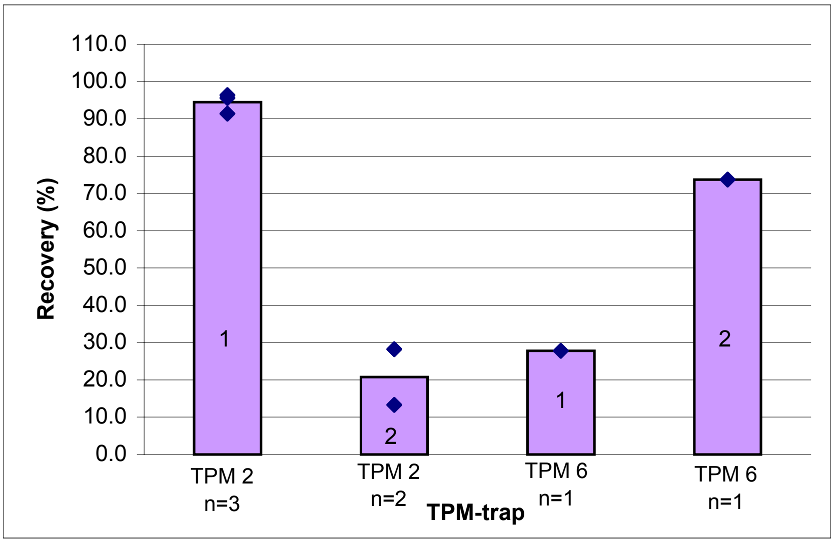

Figure 12: Tests with standard reference material on TPM 2 and TPM 6. Column 2 displays the value obtained after reconstruction of the traps. Dots indicate single values; columns give the average values.

6.7.2.1 Standard reference material – weighing procedure

Making quantitative transfers of dust material from a weighing tray (see Chapter 4.9) to the TPM-traps certainly involves risk of introducing error (e.g. loss of material), especially when the amounts in question are in the range from a few hundred to a thousand micrograms. To begin with, when experiencing various recovery values of the standard reference material added to the traps, it was suspected that the weighing procedure was the origin of the problem. Could the poor recovery values be a result of error by loss introduced when weighing out and transferring the minimal amounts of material to the traps? In order to evaluate this possibility, increased amounts (1000 to 8000 µg), of NIST 1633 b were added to different traps, thereby reducing the uncertainty linked to weighing out extremely low amounts of material. No effect was observed. Correlation analysis between the amount of NIST 1633 b and the recovery observed, were run for a further check if there were any link between these two parameters. The Pearson correlation coefficient were as low as 0.02 (n = 65).

To lower the uncertainty of the weighing procedure it would be advantageous to add the material directly to the trap and thereby weighing it out by difference. This procedure was ruled out by the fact that the mass of the TPM-trap together with a support device exceeded the range of the microbalance (max: 5100 mg, d = 0.001 mg).

6.7.3 Determination of Hg in solution on the hydride system with the MERLIN detector – intermediate precision

Having no internal calibration source, the MERLIN is simply giving a voltage response transcribed on a recorder as curves with a certain peak height (mm) and does not report a value of the mercury content. The calibration by running solutions with known concentrations of Hg is hence necessary in order to measure Hg samples and may not be applied for any evaluation of the accuracy. Still, running several replicates of the standard Hg solutions will give an impression of the precision of the analyses. The intermediate precision was tested by analysis of six series of standard Hg-solutions (at five different concentration levels) performed on three different days. Table 10 illustrates the results of the test (raw data: Appendix 2.3, Table B).

Table 10: Parameters for the determination of intermediate precision for Hg analysis performed on the MERLIN detector.

Number of parallels, N	*6*	*6*	*6*	*6*	*6*
Theoretical value (ng l^{-1})	*5*	*10*	*20*	*40*	*100*
Detector response (mm)	*7.8*	*14.0*	*28.2*	*57.0*	*139.8*
SD (mm)	*0.5*	*0.9*	*1.1*	*2.3*	*2.5*
RSD (%)	*6.8*	*6.8*	*4.0*	*4.1*	*1.8*

Despite the fact that two of the relative standard deviations slightly exceeded the 5%-limit, the intermediate precision was regarded as satisfactory.

6.7.4 Glass fiber filter method – accuracy

An accuracy test of the digestion procedure and the analytical system was performed by acid digestion of a registered amount of standard reference material (NIST 1633 b) in 10 ml HNO_3 (1:1) followed by dilution to 40 ml. The results listed in, indicate that the accuracy of this procedure was good (raw data: Appendix 2.3, Table E).

Table 11: Mercury concentration in coal fly ash (1633 b) determined after acid digestion according to the NS 4470 procedure followed by analysis on the MERLIN.

Certified value ± SD (mg kg^{-1})	*0.141 ± 0.019*
Measured value ± SD (mg kg^{-1})	*0.140 ± 0.012*
Number of parallels, N	*7*
RSD (%)	*8.6*
Confidence interval at 95%	*0.131 – 0.149*
Accuracy as recovery (%)	*99.6*

6.8 Optimisation of the wet digestion procedure

Due to the extremely low levels of particulate mercury expected to be found on the filters, it was imperative to dilute the samples as little as possible. An acid concentration of maximum 10% was recommended for the PSA 10.003 Vapour Generator, putting a limit to the HNO_3 content in the samples. The filter, cut into small pieces and transferred to Duran glasses, demanded a certain volume of acid to be covered properly in liquid and thereby secure appropriate digestion. Incomplete destruction of the filter material may lead to erroneous analytical results (Lu and Schroeder, 1999).

Clean filters added known amounts of SRM were pressure cooked in different volumes of acid to check if the digestion capacity was altered according to the volumes. Acid volumes of 12, and 20 ml diluted to 40, 60 and 100 ml respectively were tested. Figure 13 illustrates the Hg recoveries obtained using the different volumes.

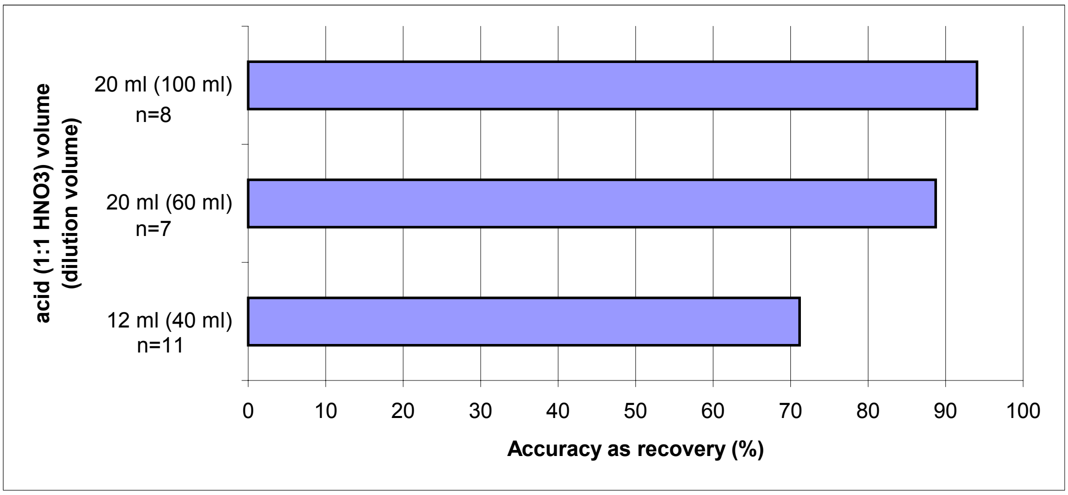

Figure 13: Recoveries of standard reference material according to various acid volumes (1:1 HNO_3) and dilution volumes.

Digestion with 20 ml acid followed by dilution to 100 ml gave the best results of 94% recovery, the 60 ml option following close with 89%, while digestion with 12 ml HNO_3 followed by dilution to 40 ml only yielded 71% recovery. More thorough washing of the digestion glass was probably the reason why dilution to 100 ml gave better recovery compared to the 60 ml option. However considering the ideal of minimal dilution, the latter procedure was preferred.

For these samples, which were digested with 20 ml HNO_3 (1:1) followed by dilution to 60 ml, the acid concentration amounted to 17%, exceeding the preferred limit of the vapour generator system. However, it was judged to be acceptable as long as each running of samples through the system was followed by long periods of cleaning (by running ultra pure water through the system).

Running series of standard Hg solutions with a HNO_3 concentration of 17 % gave similar yields as the normal standards with 1% and10% HNO_3 content, indicating that the increased concentration of acid had no noticeable effect on the analysis.

6.9 Statistical procedures

6.9.1 Correlation

Spearman's rank correlation (r_{sp}) was employed for a statistical evaluation of the reverse relationship between gaseous and particulate mercury. Spearman's correlation is non-parametric and does not require normal distribution. Calculation of the correlation coefficient, r_{sp}, is done according to equation 14. There is good correlation between two parameters (X and Y) when the value of r_{sp} is close to –1 or +1. When $r_{sp} = 0$ there is no correlation (Bhattacharyya and Johnson, 1977).

$$r_{sp} = \frac{\sum_{i=1}^{n}\left(R_i - \frac{n+1}{2}\right)\left(S_i - \frac{n+1}{2}\right)}{n(n^2-1)/12} \tag{14}$$

$-1 < r_{sp} < +1$
R = ranks of X_i
S = ranks of Y_i
n = number of measurements

6.9.2 Confidence interval

Confidence intervals were calculated according to equation 15 (Tønseth and Døhl, 1996).

$$\mu = \mathrm{X}_{\mathrm{mean}} \pm \mathrm{t} \cdot \left(\frac{SD}{\sqrt{n}}\right) \tag{15}$$

n = number of parallels
t = t-value on number of degrees of freedom (n – 1) and confidence level (P = 95%)

6.10 Ny-Ålesund TPM-trap samples – memory effect

The majority of the samples from the Ny-Ålesund fieldwork (May 2000) were analysed at NILU during September 2000. A severe memory effect was produced in the analytical system when these samples were analysed. In some cases as much as ten five minutes cycles had to be run in order to arrive at the original background level. No such memory effect was registered when analysis of samples from the Mediterranean Sea and Kjeller fieldworks was performed. All the mercury seemed to be desorbed during two heating cycles of five minutes each. As a general rule the result of each sample was set to be the yields of the two first heating cycles.

6.11 Summing up

Feasibility of sampling air directly through the TPM-traps is certainly a positive aspect of the sampling box. However further development should be performed in order to achieve improved sampling conditions, e.g. positioning of the box at an adequate height above ground level in addition to attaining metal-free surroundings.

Improvements of the TPM oven are desired in order to secure stable temperature for each TPM-trap sample analysis.

For the Hg_{part} determination with the glass fiber filter method it is reasonable to conclude that the analytical procedure (sample handling and analysis) was working satisfactorily. Both precision and accuracy were good. An evaluation of the actual sampling has not been undertaken since this method was used in previous works for TPM sampling (Berg et al., 2001) and was mainly intended as means of comparison for the TPM-trap method in this work.

The analytical system for determination of particulate mercury sampled on TPM-traps is also judged to be adequate according to accuracy and precision parameters. Though an error of systematically low yields was observed when standard injections were made through the calibration port situated at the TPM-trap site in the analytical train. It is assumed that the same "loss" of mercury also occurred when actual samples were analysed. This error was corrected for by using the calibration curve based on standard injections made at the similar site as the TPM-trap in the analytical train for calculation of results.

A severe error was identified when evaluating the TPM-trap as a sampler of particulate mercury. When applying standard reference material to a number of traps, recovery values between 13 and 102% were observed. Probably these individual differences between the traps were present also during sampling, and therefore led to various retaining of particulate matter in ambient air. It is difficult to pinpoint an exact reason for this. It is unlikely that the error is introduced during the weighing of standard reference material. When testing with greater amounts of material (thereby lessening the error by loss) no effect on the recovery linked to each trap was observed. It cannot be ruled out that error was introduced by the operator, unconsciously performing slightly different procedure from time to time. Neither can it be established that unidentified circumstances in the analytical procedure were not influencing the results. However, both the latter suggestions are improbable since a specific recovery value (within ± 20% of the average) was linked to each trap. This points to the manifestation that the problem lies within the TPM-traps. Further it is likely to assume that it is related to the construction of the trap, since the systematic error linked to each trap seemed to change when the trap was dismantled, cleaned and reconstructed with a new filter. The data material supporting the latter assumption is rather meagre. Further testing ought to be performed in order to draw any firm conclusion.

At the present stage, for reliable sampling and determination of particulate mercury, each trap would have to go through testing with standard reference material, in order to settle a specific recovery value for the trap, before usage in the field for sampling (without being repacked on beforehand). The results obtained by one trap could be corrected by multiplication with the inverse recovery value. This procedure is however tedious. In addition the presence of reference material on the filter within the trap would probably affect the sampling ability of the TPM-trap.

The sum of errors introduced in each step of an analytical method is known as the total uncertainty of the method. In the case of the TPM-trap method, a significant error is identified as individual traps yield a certain recovery at repeated tests with standard reference material. It is reasonable to deduce that these differences apply when the traps are used for sampling. This overshadows other potential errors present in the procedure and needs to be sorted out before it makes any sense to make a detailed estimation of error contributed on individual parts of the analytical procedure.

7 Results

Tables over sampling hours and TPM concentrations both for the TPM-trap method and the glass fiber filter method are listed in Appendix 3.1 – 3.3.

7.1 Ny-Ålesund

7.1.1 Sampling of TPM on TPM-traps

Due to various reasons discussed below, the results cannot be considered to give a fair picture of the TPM concentrations in the polar atmosphere and hence are not included in this chapter (raw data: Appendix 3.1, Table A-B).

7.1.2 Sampling of TPM on glass fiber filters, 142 mm

Figure 14 displays the concentrations of total particulate mercury (TPM) measured during year 2000 at the Zeppelin station, Ny-Ålesund. The values range from 0 to 46.8 pg m^{-3} with relatively stable and low values (0 – 5.8 pg m^{-3}) appearing during the period February to March as well as June to September. During April and May episodes of elevated TPM concentrations occur with two distinctive peaks taking place at the 3th and 14th of May (raw data: Appendix 3.1, Table C-D).

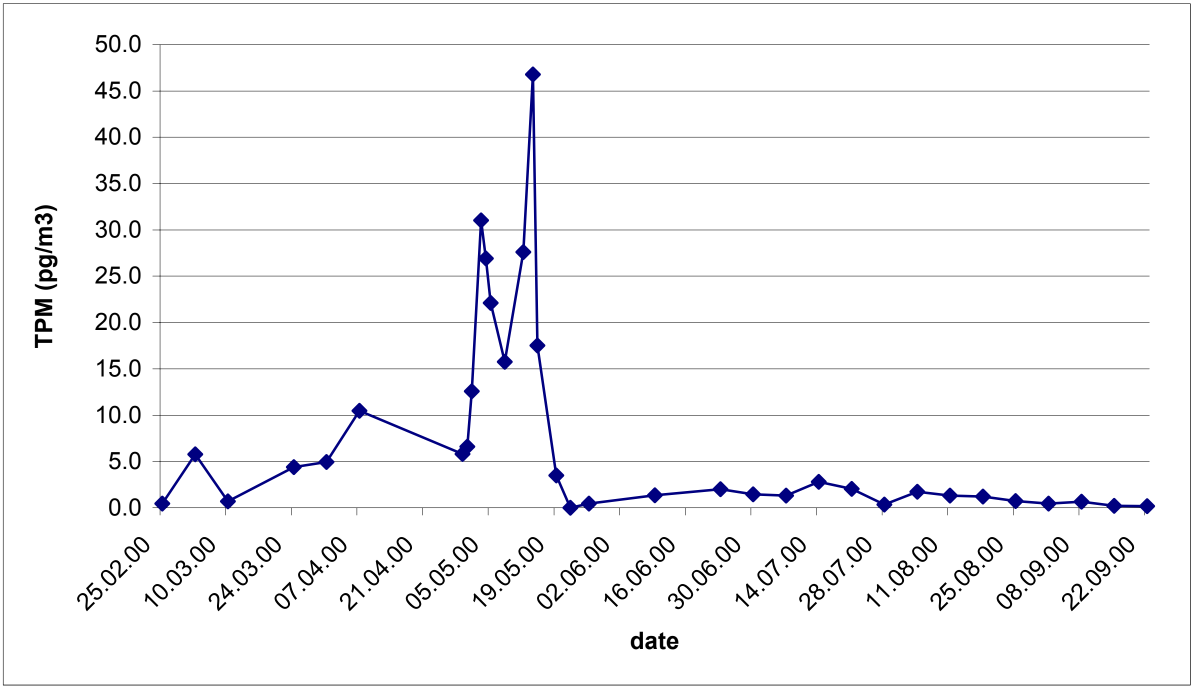

Figure 14: TPM concentrations at Ny-Ålesund from late February to September, year 2000.

7.1.3 *Comparison of total particulate mercury (TPM) values with total gaseous mercury (TGM)*[6]

In Figure 15 the TPM data (blue curve) is compared with data for total gaseous mercury (pink curve) obtained during the same period. Each TGM data point is an average value of measurements made in the equivalent period of TPM sampling. Note that the two data sets have got different scales on the Y axes.

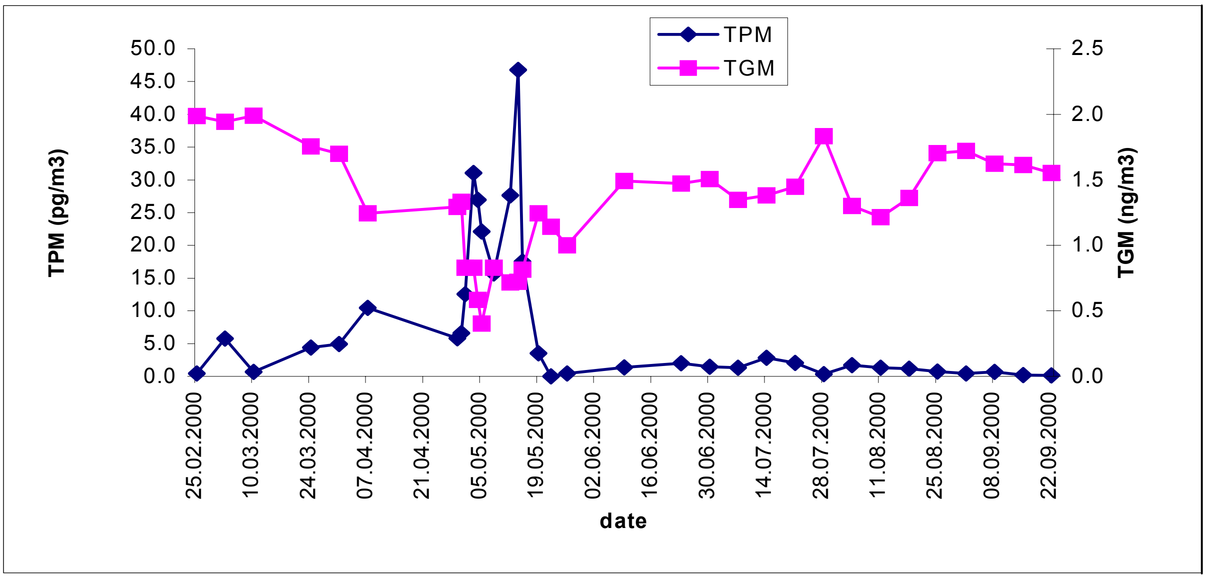

Figure 15: TPM and TGM concentrations at the Zeppelin station, Ny-Ålesund.

A Spearman rank correlation analysis run on the TPM and TGM data produced a correlation coefficient of –0.63 (significant at the 0.01 level).

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[6] The TGM raw data are delivered by T. Berg, NILU.

7.2 Mediterranean Sea

Figure 16 describes the TPM results obtained in this work compared with the TPM results produced by the Italian research group (CNR-Institute for Atmospheric Pollution) during the period from late July to the 8th of August, year 2000. Each column represents a sample made during approximately 24 hours. Raw data (this work) are listed in Appendix 3.2, Table A-B. Six out of eleven results are based on a mean value of two parallels, whereas the rest is based on one value for each day. Due to various problems with analytical systems some results were lost.

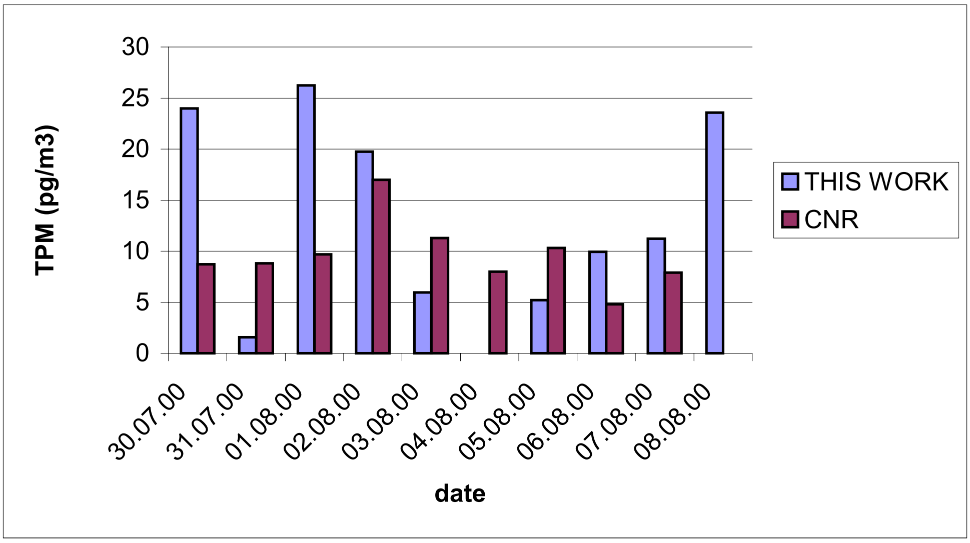

Figure 16: Intercomparison of TPM results obtained in this work and by the Italian research group (CNR) at the Mediterranean Sea.

The 4th of August the TPM concentration (this work) did not exceed the field blank value. The Italian group did not sample TPM on the 8th of August.

The main statistical parameters describing the distribution of TPM values obtained by CNR and in this work are summarised in Table 12.

Table 12: Main statistical parameters for TPM concentrations

	CNR	*THIS WORK*
Mean (pg m^{-3})	*9.6*	*14.2*
SD(pg m^{-3})*	*3.22*	*9.32*
Minimum (pg m^{-3})	*4.8*	*1.6*
Maximum (pg m^{-3})	*17.0*	*26.3*

* Standard deviation

7.3 Kjeller

Table 13 lists the ambient air concentrations of TPM sampled and determined using the TPM-trap (raw data: Appendix 3.3, Table A-B).

Table 13: Concentrations of TPM in ambient air sampled at Kjeller on TPM-traps.

start date	*N*	*sampling*	*flow rate*	*volume*	*range*	*arith. mean*	*RSD**
Year 2000		*time (h)*	*l min^{-1}*	*m^3*	*pg m^{-3}*	*pg m^{-3}*	*%*
Sept 20	*4*	*26*	*4.0 – 6.1*	*6.2 – 10.3*	*17.9 – 47.4*	*31.1*	*47*
Sept 25	*4*	*23.5*	*4.0 – 5.7*	*5.6 – 8.0*	*5.5 – 50.0*	*25.4*	*91*
Sept 26	*4*	*23.5*	*4.2 – 5.6*	*6.0 – 8.0*	*88.3 – 100.0*	*94.5*	*6*
Sept 27	*4*	*23*	*4.2 – 6.3*	*5.8 – 8.7*	*85.3 – 103.8*	*99.4*	*12*
Sept 28	*4*	*24.5*	*5.5 – 7.1*	*6.7 – 8.6*	*6.4 – 95.4*	*67.3*	*62*
Sept 29	*4*	*20*	*4.4 – 6.1*	*5.3 – 7.4*	*31.2 – 180.0*	*79.6*	*87*
Oct 4	*3*	*23*	*4.1 – 5.6*	*5.5 – 8-0*	*3.4 – 24.2*	*11.0*	*104*
Oct 5	*3*	*23.5*	*4.1 – 5.7*	*5.8 – 7.7*	*3.6 – 9.0*	*5.8*	*49*
Oct 10	*3*	*23.5*	*3.9 – 6.0*	*5.4 – 8.3*	*4.8 – 36.4*	*21.1*	*75*
Oct 11	*3*	*22.5*	*4.3 – 5.4*	*5.8 – 7.3*	*22.0 – 46.7*	*46.9*	*42*
Oct 12	*3*	*20.5*	*4.4 – 6.3*	*5.4 – 7.8*	*4.8 – 46.8*	*31.7*	*74*

* Relative Standard Deviation

7.3.1 Comparison of results obtained from the TPM-trap method and the glass fiber filter method

In addition to sampling of TPM on TPM-traps, particulate mercury was also collected on glass fiber filters installed in high volume samplers. Figure 17 shows plots of the TPM concentrations obtained by the two different sampling methods along a time axes (September and October 2000). Each column represents a sample made during approximately 24 hours (raw data: Appendix 3.3, Table A-C).

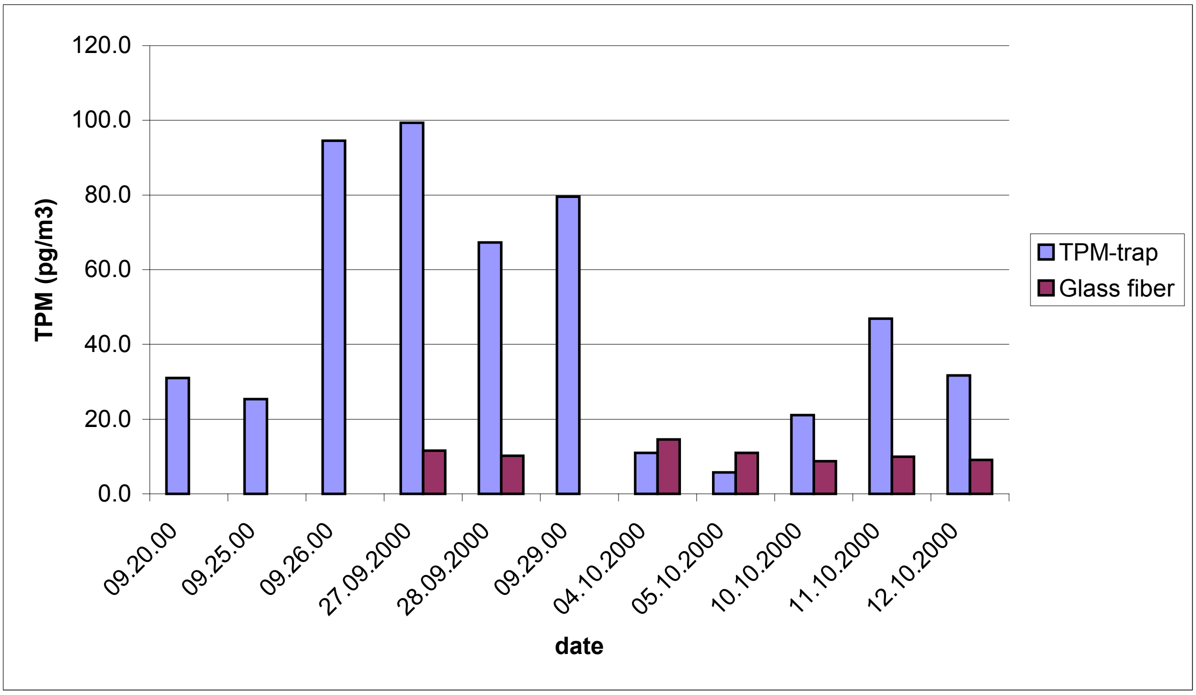

Figure 17: Comparison of TPM concentrations sampled by two different methods

8 Discussion

8.1 Ny-Ålesund

8.1.1 Sampling on TPM-traps

Eleven TPM samples were analysed within a couple of days after end of sampling at the Zeppelin station. The results were judged to be poor for a couple of reasons. It turned out to be difficult to make a decent calibration curve on the system. Especially the precision was poor; repeated injections of 102 pg Hg° gave successive results of 103, 25, 71, and 109 pg. This was not a rare incident. However, the system being on hand, a few samples were run. The results obtained were not in the expected range. With the exception of one sample, the yields were exceptionally low. It was particularly disturbing that the majority of the samples did not exceed the background level of the blanks. Lack of a reliable calibration curve together with the “strange” yields obtained, made the reliance of these results questionable. It was found advantageous to store the remaining samples until a trustworthy analytical system was available.

The remainder of the Ny-Ålesund TPM-trap samples were analysed in September 2000 on a set-up with the TEKRAN 2537A analyser. The results produced were generally far above the expected range, often in the order of one hundred times greater. Extremely high blank values excluded the assumption that these values reflected the natural TPM level in the polar atmosphere. Only exposure to some kind of contamination during the line of events could possibly explain the magnitude of these yields. Comparison with the results obtained from the analysis with the GARDIS system at Ny-Ålesund producing low yields, could point to the fact that the contamination must have been added during the period of storage. The samples were stored for approximately four months, however all the time properly sealed with teflon stoppers and packed in double rubber bags. It is hard to understand where or when a possible contamination could enter the allegedly stopped traps, but this possibility cannot be excluded.

When only TEKRAN data were considered, the average of the blank trap results was 2215 pg Hg, while the average of the sample results was 1244 pg Hg (absolute values), almost one nanogram lower than the blank average. This observation could imply that the traps were exposed to a point source of Hg during preparations of the traps at the Zeppelin station (e.g. during the few minutes of cooling after the traps were cleaned by heating). From the traps used for sampling possible contamination could evaporate during the sampling period of 24 or 48 hours and hence give the lower results compared to the blank traps which were open to the surroundings only for a few minutes. Still it is difficult to point to an exact source of this possible pollution. And the extremely low results produced from the analysis on the GARDIS (though judged not to be reliable) are hard to reconcile with the presence of a source of Hg within the Zeppelin station building.

Another explanation of the elevated TEKRAN results could be that Hg contamination was added during the sample handling (e.g. unpacking) just prior to analysis at the NILU laboratory. However, the analysis of test samples and samples from other fieldworks performed in similar a manner, yielded “normal” results and hence makes this proposal improbable.

The TEKRAN being a selective Hg detector could not possibly give such results as a response to interferences (D. Scneeberger, pers. comm.). Anyway this alternative was checked, but the output curves displayed single peaks appearing at the Hg line.

It seems difficult to explain these results. Somewhere in the line of events considerable amounts of mercury must have been added to the traps. How and when are questions desirable to answer but at the present only possible to approach with suggestions. The long period of storage should in theory be no problem (I. Wangberg, pers. comm.) but it makes the list of potential interferences longer. It would be advantageous to be able to perform analysis immediately after the end of a sampling period. A possible contamination would be detected and the problem could be addressed without delay.

8.1.2 Sampling of TPM on glass fiber filters

Figure 14 displays a distinctive pattern of elevated TPM concentrations during the month of May. Throughout the rest of the year the level is relatively stable and low. This is consistent with the theory suggested that TPM is formed during the months following polar sunrise (Schroeder et al, 1997; Lu et al., 1998; Schroeder et al., 1998). According to the same theory total gaseous mercury (TGM) should display an inverse pattern of depletion episodes. Figure 15 shows a comparison of TPM and TGM values between February and September 2000.

8.1.2.1 Blanks

During the periods from February to April and late May to September only three blank filters were produced (average: 94 pg Hg), whereas during the period of the fieldwork four blank samples were obtained (average 619 pg Hg). The great difference between these two blank values may be explained by different procedures when it comes to the handling of the filters. The fieldwork blanks produced during May were unwrapped, installed in the sampler, dismantled, and wrapped in the aluminium foil, whereas the three blanks from the rest of the year did not go through these steps; they were only transportation blanks. The elevated blank values from the fieldwork may indicate that the filters are exposed to some kind of contamination during the sample handling steps. More tests should be taken over a time period to identify a possible source. Still the fieldwork blanks seem to be unexpectedly high as the average exceeds some of the sample values. The samples obtained from the fieldwork were corrected with the blank value of 619 pg Hg while the remaining samples were subtracted 94 pg Hg. The correction, though extraordinary high for the fieldwork samples, had minor influence on the pattern of peak episodes appearing during the month of May. The low number of blanks is blameworthy and represents a weakness of the quality of the data set.

8.1.3 Comparison of total particulate mercury (TPM) values with total gaseous mercury (TGM)

Clearly TGM depletion episodes occur (Figures 1 and 15) and to a large extent they coincide with the TPM peaks. For the TPM top occurring at the 3rd of May (31 pg m^{-3}), the corresponding TGM decrease seems to be delayed with a minimum occurring at 5th of May. In addition the depletion of TGM corresponding to the TPM peak at the 14th of May (49 pg m^{-3}) is not as pronounced as the depletion corresponding to the 3rd of May peak, though the opposite situation would be expected. The correlation (r_{sp} = -0.63) between the two mercury species further implies that a perfect inverse co-variation between TPM and TGM is not present in these data sets. Still the data clearly indicate that TGM is depleted while TPM is present at elevated values during this period following polar sunrise, pointing to the occurrence of reactions where elemental gaseous mercury is transformed to oxidized species such as particulate mercury and gaseous divalent mercury. Ozone, hydroxyl radicals chlorine, and bromine have been suggested to oxidize the Hg° to Hg^{2+} transformation (Pleijel and Munthe, 1995; Lin and Pehkonen, 1999; Lindberg et al., 2000).

A more accurate picture of the correlation between TPM and TGM would be obtained if particulate mercury sampling were performed during shorter intervals giving an increased time resolution. The ambient air TGM concentration monitored every five minutes at the Zeppelin station during spring time (Figure 1), revealed that depletion episodes may occur during short time intervals of only a couple of hours. Distinctive episodes get “drowned” when averages over longer time periods are taken. However, when implementing the TPM-trap method for the first time during spring 2000, the main consideration was to secure a detectable amount of particulate mercury on the TPM-trap. The glass fiber filters were sampled at similar time intervals to obtain a good comparison.

8.2 Mediterranean Sea

The range of atmospheric TPM concentrations in the Mediterranean area was expected to be 10 – 50 pg m^{-3} (N. Pirrone, pers. comm.). The data obtained during the fieldwork was in the lower half of this range, with a maximum value of 26.3 pg m^{-3}. The parallels (obtained for six of the eleven sampling days, see Appendix 3.2) were equivalent for the 1st and the 8th of August. The remaining varied somewhat, which may be related to the individual differences between the traps as pointed out in chapter 6.7.2.

The Italian results were on average lower than the results obtained in this work, producing means for the whole period of 9.6 pg m^{-3} and 14.2 pg m^{-3} respectively. However there is no consistent pattern with Italian values being a certain percentage lower than the data of this work. The situation is quite the opposite with the Italian data sometimes higher sometimes lower than the data of this work. In addition the Italian results are quite stable during the period, giving a standard deviation of 3.22 pg m^{-3} whereas the data generated in this work were fluctuating from day to day between the upper and lower part of the range (SD = 9.32 pg m^{-3}). It is difficult to judge which set of results is the most reliable, as the TPM concentrations are known to vary both between sites as well as from day to day. The differences may be due to natural variations occurring as a consequence of different positioning of sampling units. The uncertainties in the methods probably surmount the differences observed. Still the Italian group, being more experienced, should get the credit of being “most trustworthy”. In addition the results from tests with standard reference material pointing to a severe systematic error present in the TPM-sampler makes it appropriate to put a question mark behind the results of Hg_{part} obtained by sampling on TPM-traps.

8.3 Kjeller

8.3.1 Sampling on TPM-traps

For the fieldwork made during a fortnight in September and October, year 2000, the TPM values ranged between 5.8 and 99.4 pg m^{-3}. No earlier measurements of particulate mercury have been made in this area, and hence there is little knowledge of which level to expect. In the literature ambient air TPM concentrations in urban/industrialized areas are reported in the range from 86 to more than 1000 pg m^{-3} whereas rural values are in the order of 10 to 30 pg m^{-3} (Keeler et al, 1995; Lu et al., 1998; Pirrone et al., 1995). Kjeller is a suburb situated 20 km northeast of Oslo and relatively heavy traffic is passing at a distance of 100 – 200 meters from the sampling site. A total average of the period amounting to 46.7 pg m^{-3} seems like a reasonable value when keeping the position of the sampling site and literature values in mind.

A general trend evident when looking at each sampling batch consisting of 3 or 4 parallels is the spread within each data set (Table 13). After omitting possible outliers, the relative standard deviation still amounts to 91% for one of the batches and is approximately 50% for four of the other batches. This is far too much and is a disturbing element of the quality of the data. It cannot be entirely ruled out that the variation observed is due to inhomogeneity of particulate mercury in ambient air, though this is not seen in the literature (Lu et al., 1998), neither in the parallels sampled on glass fiber filters (this work).

The traps are positioned at slightly different spots (two traps in the sampling box and two traps in separate sampling units poking 1.5 meters out from the wall), hence the experimental conditions are slightly different for each trap which could justify small deviations between the parallels, nevertheless the variation seen in these results are hard to explain from this approach. Local contamination cannot be ruled out as a possible cause of the differences. However there are no systematic discrepancies between the results obtained from the traps sampling in the box and those traps sampling in the sampling units on the wall.

The flow rates of the air sucked through the traps vary (min: 3.8 $l\ min^{-1}$; max: 6.6 $l\ min^{-1}$). One hypothesis could be that traps sampled with higher flow rates retain less particulate mercury compared to those sampled at lower flow rates due to evaporation of associated Hg°. Running a correlation analysis between sample concentrations and flow rates rules out any such relation. The issue of evaporation of mercury from the sample should nonetheless be taken into account when considering sampling at significantly higher flow rates, such as for the glass fiber filter method.

The large differences observed between the parallels led to extensive testing with standard reference material in order to detect any possible patterns related to the traps. The results of these tests are listed and discussed in Chapter 6.7.2, and it was concluded that each individual trap give a certain recovery when testing with standard reference material. If the same mechanisms producing the great variety between these traps apply to actively sampling traps, it is likely to conclude that the samples giving the higher yields in the batch are the most reliable ones. However, again it is risky to draw any firm conclusions as the cause of the poor sampling parallels may be linked to local pollution or other unforeseen sources.

8.3.2 Comparison of two sampling methods

Particulate mercury is an “unsteady” species when it comes to measuring the exact quantum of it. Since Hg° can be loosely associated, the TPM quantum may be reduced or increased during sampling hours by evaporation and sorption respectively. It is reasonable to deduce that different sampling methods employing diverse flow rates and filter material may have an effect on the fraction of particulate mercury actually sampled.

Clearly the results obtained by using the TPM-trap method is considerably higher than those obtained from the glass fiber filter method. Only the samples made on the 4th and 5th of October are in the same size order (TPM-trap: 11.0, 5.8 pg m^{-3}; glass fiber: 14.5, 10.6 pg m^{-3} respectively). These are the only samples where the glass fiber method gave higher results than the TPM-trap method. Otherwise the TPM-trap results are two to nine times higher than the glass fiber filter results. This difference could be due to diverse experimental conditions, random errors or systematic errors.

Dealing with samples with such minuscule amounts of the analyte makes the procedure incredibly sensitive to pollution. The divergence between the two sampling methods may be an effect of different positioning of the air sample inlets; the glass fiber method sampled air through pipes on the roof of the sampling hut, reaching approximately 4 meters above ground level, while the TPM-traps had air inlets only 1.7 meters above the ground. It is reasonable to think that the latter could be exposed to ground related “pollution”, which could cause the higher yields.

The two methods, though built on the same principle, have got different experimental conditions and procedures. Among other things does the composition of the filter material differ between the two. The TPM-trap contains a quartz fiber filter with a pore size of 0.3 µm, whereas the glass fiber filter has a pore size of 1.0 µm. Hence TPM-traps collects the size fraction between 0.3 and 1.0 µm, which eludes the glass fiber filter. TPM-trap results are consequently expected to be higher, to which extent depends on the size distribution of particulate mercury at the specific time and site. Another factor, which possibly causes divergence, is the flow rate of the air which is sucked through the filters. The glass fiber filter is sampling at a flow rate, which is 15-20 times higher than the flow rate pulled through the TPM-traps. It has been suggested that this higher flow rate (~6 m^3 h^{-1}) may entail volatilisation of mercury species associated with particles collected on the glass fiber filters and hence produce systematically lower results compared to the TPM-traps (Lu et al., 1998; Berg et al. 2001). The data set (Table 13, Figure 17 and Appendix 3.3, Table C) is quite limited. Further investigation would be needed in order to fully understand this potential sampling artefact.

9 Conclusions and suggestions for further work

A considerable part of the work behind this thesis consisted of acquiring and constructing necessary apparatus for the determination of particulate mercury sampled on TPM-traps. A custom-made sampling box and a TPM-oven were constructed in collaboration with the Department for Instruments and Field Sampling at NILU. In addition the various materials constituting the TPM-trap were required. The construction of the trap turned out to be a challenge, eventually overcome by the revelation of the expansion tong.

The further work was characterized by problems with establishing a reliable analytical system for the determination of particulate mercury on TPM-traps. Due to various circumstances two fieldworks were undertaken without a reliable analytical system available for analysis of the samples. The fact that such a system was lacking also impaired method evaluation/ optimisation tests desirable to be accomplished before the TPM-traps were used for sampling.

In order to detect the presence of elevated particulate mercury values during the period following polar sunrise at Ny-Ålesund, measurements had to be undertaken before the end of May. The TPM-trap was based on a model already in use by a Swedish research group, and its constituents were even manufactured by the same glass blower. At the time being it was assumed that the TPM-trap was an adequate sampler of particulate mercury, an assumption made too hastily as it should turn out later.

The Mediterranean research cruise during the first half of August 2000, was considered to be a unique possibility to work with, and hopefully learn from, experienced researchers dealing with ambient air mercury measurements. It would serve as a great opportunity of comparing TPM results obtained in this work with results produced by the Italian research group undertaken with an identical method.

Planning and preparing these fieldworks was time consuming and probably delayed the process of obtaining a functioning analytical system, although continuous efforts were made in between as well as during these field studies.

Not until September 2000 however was a functioning system achieved, as a TEKRAN mercury monitor was temporarily available at the laboratory at NILU. Samples from Ny-Ålesund and the Mediterranean Sea were finally analysed. In addition field measurements were made outside the NILU quarters with three or four sampling parallels. The considerable variation between these parallels was puzzling. Extensive testing of the TPM-traps with standard reference material eventually made it evident that the TPM-traps possessed individual differences not compatible with performing reliable measuring of TPM with these samples.

The following conclusions and suggestions for further work may be extracted from this thesis:

In the future further development of the sampling box should be undertaken in order to obtain cleaner and more stable conditions during sampling. A system for hoisting and lowering the box on a pole is proposed to achieve adequate distance between the sampler and potential contaminants such as metal material, painted walls etc. Also improvements of the custom-made TPM oven would be adequate to obtain stable experimental conditions for successive TPM-trap samples.

Further investigation of the TPM-trap as a sampler for particulate mercury has to be performed in order to identify the cause(s) of the differences observed between the individual traps. Only when this is accomplished and corrected for, may the TPM-trap be implemented as an adequate method for collecting $Hg_{part.}$ It is likely to assume that the problem is related to the construction of the trap, since the systematic error linked to a specific trap seems to change when it is reconstructed with a new filter. The data material supporting the latter assumption is rather meagre. Further testing ought to be performed in order to draw a firm conclusion.

At the present stage, a possible approach for the sampling and determination of particulate mercury, would be to perform testing with standard reference material on each trap, in order to settle a specific recovery value, before usage in the field for sampling (without being repacked on beforehand). The results obtained by one trap could be corrected by multiplication with the inverse recovery value. This procedure is however tedious. In addition the presence of reference material on the filter within the trap would probably affect the sampling ability of the TPM-trap.

In the hypothetical case of possessing a satisfactorily operating TPM-trap method, it would be interesting to undertake tests with several traps in series in order to establish any possible breakthrough of particulate matter. An adjustment of the flow rate might be proved necessary. Due to the problems with the TPM-trap mentioned above, performing such tests was found not to be essential at the time being.

When the work with this thesis was initiated the glass fiber method was regarded as means of obtaining results representing a “true” level of Hg_{part}. However, as further experience with this method was obtained, questions concerning the reliability of it were raised. The results were consequently lower than the expected range pointing to a possible artefact in the method. In the future, experiments should be performed in order to assess this method thoroughly. Among other things it would be interesting to run tests with several filters in series to check any possible breakthrough of particulate mercury.

The high field blank levels obtained with the glass fiber filter method should also be an issue of concern. Investigation of the procedure in order to identify and minimize the contributions of contamination during the field sampling handling steps would be desirable to obtain better sensitivity and lower detection limit of this method.

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Appendix

Appendix 1.1

List of chemicals:

Chemical	*Purity*	*Brand*	*Application*
Nitric acid, HNO_3	*Suprapure, 65%*	*Merck, Eurolab*	*Digestion*
Nitric acid, HNO_3	*Pro analysi, 65%*	*Merck, Eurolab*	*Cleaning*
Hydrochloric acid, HCl	*Suprapure, 30%*	*Merck, Eurolab*	*Various solutions*
Tin(II)chloride-2-hydrate, $SnCl_2$	*Pro analysi,* *max 0.000001% Hg* *> 98%*	*Merck, Eurolab*	*Reducing agent in the analysis of Hg in solution*
Potassium bromide, KBr	*Pro analysi,* *> 99.5%*	*Merck, Eurolab*	*Br-Cl solution*
Potassium bromate, $KBrO_3$	*Pro analysi,* *> 99.8%*	*Merck, Eurolab*	*Br-Cl solution*
Ultra clean water, MilliQ plus	*Conductivity: $< 0.5\ \mu S\ cm^{-1}$*	*Millipore Corp., USA*	*Dilution, washing.*
Standard reference material:	*Trace Elements in Coal Fly Ash, 1633 b, Hg: $0.141 \pm 0.019 mg\ kg^{-1}$*	*NIST, USA*	*Method validation*
Standard solution of Hg:	*$10\ \mu g\ ml^{-1}$* *(UL ISO 9001 Quality Assurance System)*	*SPEX Certiprep, Inc., USA*	*Calibration*
Compressed argon, ultra plus 6.0	*99.9999%*	*Hydrogas Norge AS*	*Carrier gas in Hg_{part} determination*
Synthetic air, 5.0	*99.999%*	*Hydrogas Norge AS*	*Carrier gas in Hg_{part} determination*

Appendix 1.2

Reagent procedures:

Tin(II)chloride solution

20 g $SnCl_2$ x $2H_2O$ is solved in a mixture of 150 ml HCl and 300 ml ultra clean (MilliQ plus) water. This is diluted to 1000 ml by ultra clean water. Before application the solution is aerated with argon gas for 20 minutes in order to reduce trace level mercury in the solution.

Br-Cl solution

Potassium bromate ($KBrO_3$) in a porcelain dish is heated for 24 hours in a ceramic oven at 250 ± 20°C. Potassium bromide (KBr) is heated at 300 ± 20°C for 24 hours. 11.0 g $KBrO_3$ and 15.0 g KBr are added 200 ml ultra clean (MilliQ plus) water. This mixture is blended (by a magnet stirrer) for 1 hour before 800 ml HCl is added little by little. This procedure must be undertaken In a ventilation hood due to the formation of halogens (Cl_2, Br_2) in this process.

Calibration standards:
Standard solution of Hg:
10 µg ml^{-1}

Stock standard:
2 ml Br-Cl solution and 5 ml HCl is added to 1.0 ml of the primary Hg solution. This is diluted to 1000 ml with ultra clean water (MilliQ plus). The secondary standard contains 10 ng ml^{-1} Hg and is remade every four months.

Working standards:
0.050 ml of the secondary standard is added 1 ml Br-Cl and either HCl or HNO_3 (1-10 ml) according to the matrix content in the actual samples. This solution is diluted to 100 ml and constitutes a working standard of 5 pg Hg ml^{-1}. The same procedure is used for making working standards of 10, 20, 40 and 100 pg Hg ml^{-1}. Working standards are made new every day of analysis.

List of instruments and materials:

Instrument/material	***Specifications***	***Producer/Supplier***	***Application***
Autoinjector	*Gilson 222*	*Biolab A/S, Risskov, Denmark*	*Analysis of Hg in solution (glass fiber filter method)*
Calibration Unit	*Model 2505 Mercury Vapour Calibration Unit*	*Tekran Inc., 132 Railside Road, Unit 1, Toronto, Ontario M3A 1A3, Canada*	*Calibration of analytical system*
Clean room facilities	*USFS 209E class 10 000 (10 000 particles per square feet)*	*CM Ultraclean, Spydeberg, Norway*	*Cleaning procedures Analysis of TPM (glass fiber filter method)*
Distilled water	*Milli-Q plus water purification system, 220V/50Hz, Compact. Conductivity < 0.5 μS/cm*	*Millipore Corperation, Bedford, Massachusetts, USA*	*Cleaning Dilution*
Duran flasks with teflon coated caps	*100 ml*	*Merck, Eurolab*	*Acid digestion of glass fiber filters*
Electrical heater	*Type EHZ 110-265 V 60 W*	*Pfannenberg Elektro-Spezialgerätebau GmbH, Hamburg, Germany*	*In sampling box*
Electrical heater temperature control	*Type ETR Open: 10A, 250V Close: 5A, 250V*	*Stego Elektrotechnik GmbH, Schwabisch Hall, Germany*	*In sampling box*
Expansion tong		*ELFA*	*TPM-trap construction*
Funnels	*High density polyethylene*	*Dyno Plast Limited, Kongsvinger, Norway*	*Sampling inlet shields*
GARDIS detector	*GARDIS-1A Atomic Adsorption Mercury Vapour Analyzer Detection limit: 0.5 pg*	*Ecological Spectroscopy Lab., Institute of Physics, Gostauto 12, Vilnius 2600, Lithuania,*	*Analysis of TPM samples (TPM-trap method)*
Gas meters, REMUS 3		*Schlumberger LTD*	*Sampling (TPM-trap method)*
Gas tight syringes	*1800-series, disposable needle, gas tight with handle*	*Hamilton Bonaduz AG, Bonaduz, Switzerland*	*Standard injections of saturated Hg-air. Calibration*
Gloves	*Particle free, disposable*	*Selfatrade AB, Spånga, Sweden*	*Used during handling of TPM-traps and glass fiber filters*
Gold threads	*85/15 - Ag/Pt alloy*	*Rasmussen, Hamar, Norway*	*Analytical Gold trap (MERLIN) Protective gold trap in analytical system*
High volume samplers	*Stationary units at the Zeppelin Station and at Kjeller*	*I-lab, NILU*	*Sampling of TPM on glass fiber filters*

Instrument/material	***Specifications***	***Producer/Supplier***	***Application***
Hollow punch	*Diameter: 10 mm*	*Boehm, France*	*TPM-traps (punching quartz fiber filters, 10 mm)*
Intergrator	*Dionex 4270 Intergrator*	*Dionex, California, USA*	*Preliminary determination of TPM Coupled to MERLIN detector*
MERLIN detector	*PSA 10.023 Merlin Detector*	*P. S. Analytical Ltd., Arthur House, Crayfields Industrial Estate, Main Road, Orpington, Kent BR5 3HP, UK.*	*Analysis of TPM samples (glass fiber filter method)* *Preliminary tests for the analysis of TPM samples on TPM-traps*
Microbalance	*Mettler MT5* *Max 5.1 g, d=0,0001* *(ISO 9001, EN 29001)*	*Mettler, Greifensee, Switzerland*	*Weighing out standard reference material*
Micropipettes	*100-1000 µl, 1-5 µl and 2-10 µl*	*Finnpipette Digital, Helsinki, Finland*	*Preparing Hg standard solutions* *Hg in solution samples (glass fiber filter method)*
Multimeter and heat sensor	*Fluke 73, series II* *80 TK Thermocouple module, Fluke* *Heat sensor.*	*multimeter* *John Fluke MFG, Co., Inc., Eindhoven, The Netherlands*	*Controlling the temperature of the TPM oven and pyrolyzer oven*
Nickel screen support	*Diameter: 10 mm*	*Microponent AB, Vænabo, Sweden*	*TPM-traps* *Filter support*
Peristaltic pump	*Gilson Minipuls 3 (model M 312)*	*Biolab A/S, Risskov, Denmark*	*Analysis of Hg in solution (glass fiber filter method)*
Polyethylene bags	*Minigrip*	*Christiania Æske AS Raufoss, Norway*	*Storing TPM-trap and glass fiber filter samples*
Polyethylene tubing	*Elastollan®* *Inner/outer diameter: 6/8 mm*	*BASF corporation*	*Connecting pumps and TPM-traps during sampling*
Pressure boiler		*Høyang Polaris a.s.*	*Acid digestion of glass fiber filters*
Pumps (vacuum linear stamp pumps)	*Maximum vacuum: 680 mbar* *maximum air flow: 7 l min^{-1},* *frequency: 50 Hz*	*Nitto Kohki CO., LTD*	*Sampling (TPM-trap method)*
Pumps	*ELMO 2BH5*	*Siemens*	*Sampling of TPM on glass fiber filters*
Quarts tubes, small	*Vitreosil clear fused quarts tubing, Flame fused quarts Ingot.* *Size: length 15 cm, i.d. 5 mm, o.d. 7 mm*	*Quarts from:* *Saint-Gobain Quarts PLC, Wallsend, UK* *Tubes prepared by:* *JM Glassteknikk Skandinavia AS, Oslo,Norway*	*Pyrolyzer tube* *Gold traps*

Instrument/material	***Specifications***	***Producer/Supplier***	***Application***
Quartz fiber filter	*Munktell, sheet 360, 203 x 254 mm* *Pore size: 0.3 µm* *Max temperature: 950°C*	*Munktell filter, Grycksbo, Sweden*	*TPM-traps*
Recorder	*BBC, servoger 120, goer 2* *Metrawatt, max 250 V*		*Glass fiber filter method* *Coupled to the MERLIN detector*
Sample glasses with polyethylene snap cap	*White glass* *Height: 72 mm* *Diameter: 28 mm*	*Merck, Eurolab*	*Glasses for Hg in solution samples (glass fiber filter method)*
Septum	*Ice Blue Septa, silicone septum,* *9.5 mm*	*Restek Corporation, Bellefonte,* *USA*	*Septum in calibration port on analytical system*
Silicon tubing,	*Inner/outer diameter: 9/13 mm*	*Merck, Eurolab*	*TPM-trap:* *Trap connection* *Fitting in analytical train*
Teflon connection	*Right end: outer diameter 6.5 mm* *Left end: outer diameter 10 mm*	*I-lab, NILU*	*Connecting the TPM-trap to the rest of the analytical train*
Teflon tubing	*Clear FEP, 4,78/6,35 (correspond to ¼ x 1/16 inches)*	*Furon,* *Mickleton, New Jersey,* *USA*	*Tubing for analytical line*
Teflon union tee	*TFE-Union Tee, 1/4”*	*Swagelok Corperation,* *Solon, Ohio,* *USA*	*Calibration port*
TEKRAN detector	*model 2537A, Hg monitor*	*Tekran Inc., 132 Railside Road, Unit 1, Toronto, Ontario M3A 1A3, Canada*	*Analysis of TPM samples (TPM-trap method)*
TPM-trap quartz tubes *(custom-made)*	*i/o diameter:* *outer tube 10/13 mm* *inner tube: 8/10 mm*	*Scientific-Lab. Glass AB, Löberöd, Sweden*	*TPM-traps*
Tube fittings, brass	*Brass* *1/4”*	*Swagelok Corperation,* *Solon, Ohio,* *USA*	*Connecting tubing on inside and outside of sampling box*
Two-oven system	*prototype*	*Inventory number 5576, NILU*	*Preliminary determination of TPM*
Viton tubing	*Inner/outer diameter: 6/9 mm* *9/13 mm*	*Merck, Eurolab*	*Tubing for analytical line* *Fittings in sampling and analytical line*
Vapour Generator	*PSA 10.003*	*P. S. Analytical Ltd., Arthur House, Crayfields Industrial Estate, Main Road, Orpington, Kent BR5 3HP, UK.*	*Generating Hg vapour from Hg in solution samples (glass fiber filter method)*

Appendix 1.4

Contents of TPM-oven:

Material	***Specifications***	***Brand***
Oven case:	*Extruded aluminium profile and fuel painted steel plates* *Type: Mocain 3U 42HP*	*Knürr AG, Munich*
Transformer	*Effect 600 VA at 48 to 60 Hz, 230 VAC in 2x 24 VAC out*	*Toroid International (supplied by ELFA)*
Timer	*Type: H3DE-M2 .*	*Omron Europe B.V. (supplied by ELFA)*
Heating coil	*21 turns, diameter 13 mm. Total resistance: 2.5 ohm*	*Kanthal Nikrothal AE (supplied by ELFA)*
Fan	*Papst, type 8850 N, 220 V ~50 Hz.*	*Papst Motors, St. Georgen, Germany*

Appendix 1.5

Saturated mercury concentrations versus temperature (Tekran inc.):

Temp °C	pg µl^{-1}	Temp °C	pg µl^{-1}	Temp °C	pg µl^{-1}	Temp °C	pg µl^{-1}	Temp °C	pg µl^{-1}	Temp °C	pg µl^{-1}
5.0	3.519	9.5	5.308	14.0	7.903	18.5	11.619	23.0	16.879	27.5	24.243
5.1	3.552	9.6	5.356	14.1	7.972	18.6	11.717	23.1	17.017	27.6	24.435
5.2	3.585	9.7	5.405	14.2	8.041	18.7	11.816	23.2	17.157	27.7	24.630
5.3	3.619	9.8	5.453	14.3	8.112	18.8	11.916	23.3	17.297	27.8	24.825
5.4	3.552	9.9	5.502	14.4	8.182	18.9	12.017	23.4	17.439	27.9	25.022
5.5	3.686	10.0	5.552	14.5	8.254	19.0	12.118	23.5	17.581	28.0	25.221
5.6	3.720	10.1	5.602	14.6	8.325	19.1	12.220	23.6	17.725	28.1	25.420
5.7	3.755	10.2	5.652	14.7	8.398	19.2	12.323	23.7	17.870	28.2	25.622
5.8	3.790	10.3	5.703	14.8	8.471	19.3	12.427	23.8	18.016	28.3	25.824
5.9	3.825	10.4	5.754	14.9	8.544	19.4	12.531	23.9	18.163	28.4	26.029
6.0	3.860	10.5	5.806	15.0	8.619	19.5	12.637	24.0	18.311	28.5	26.234
6.1	3.896	10.6	5.858	15.1	8.693	19.6	12.743	24.1	18.460	28.6	26.442
6.2	3.932	10.7	5.910	15.2	8.769	19.7	12.850	24.2	18.610	28.7	26.650
6.3	3.968	10.8	5.963	15.3	8.845	19.8	12.958	24.3	18.761	28.8	26.860
6.4	4.005	10.9	6.016	15.4	8.921	19.9	13.067	24.4	18.914	28.9	27.072
6.5	4.042	11.0	6.070	15.5	8.998	20.0	13.176	24.5	19.068	29.0	27.285
6.6	4.079	11.1	6.124	15.6	9.076	20.1	13.286	24.6	19.222	29.1	27.500
6.7	4.117	11.2	6.179	15.7	9.155	20.2	13.398	24.7	19.378	29.2	27.716
6.8	4.155	11.3	6.234	15.8	9.234	20.3	13.510	24.8	19.535	29.3	27.934
6.9	4.193	11.4	6.289	15.9	9.313	20.4	13.622	24.9	19.694	29.4	28.154
7.0	4.232	11.5	6.345	16.0	9.393	20.5	13.736	25.0	19.853	29.5	28.375
7.1	4.271	11.6	6.402	16.1	9.474	20.6	13.851	25.1	20.014	29.6	28.597
7.2	4.310	11.7	6.459	16.2	9.556	20.7	13.966	25.2	20.175	29.7	28.821
7.3	4.349	11.8	6.516	16.3	9.638	20.8	14.083	25.3	20.338	29.8	29.047
7.4	4.389	11.9	6.574	16.4	9.721	20.9	14.200	25.4	20.502	29.9	29.275
7.5	4.429	12.0	6.632	16.5	9.804	21.0	14.318	25.5	20.668	30.0	29.504
7.6	4.470	12.1	6.691	16.6	9.889	21.1	14.437	25.6	20.834	30.1	29.734
7.7	4.511	12.2	6.750	16.7	9.973	21.2	14.557	25.7	21.002	30.2	29.966
7.8	4.552	12.3	6.810	16.8	10.059	21.3	14.678	25.8	21.171	30.3	30.200
7.9	4.594	12.4	6.870	16.9	10.145	21.4	14.800	25.9	21.342	30.4	30.436
8.0	4.636	12.5	6.931	17.0	10.232	21.5	14.923	26.0	21.513	30.5	30.673
8.1	4.678	12.6	6.992	17.1	10.319	21.6	15.046	26.1	21.686	30.6	30.912
8.2	4.721	12.7	7.054	17.2	10.407	21.7	15.171	26.2	21.860	30.7	31.153
8.3	4.764	12.8	7.116	17.3	10.496	21.8	15.296	26.3	22.035	30.8	31.395
8.4	4.807	12.9	7.179	17.4	10.586	21.9	15.423	26.4	22.212	30.9	31.639
8.5	4.851	13.0	7.242	17.5	10.676	22.0	15.550	26.5	22.390	31.0	31.885
8.6	4.895	13.1	7.306	17.6	10.767	22.1	15.679	26.6	22.569	31.1	32.133
8.7	4.939	13.2	7.370	17.7	10.859	22.2	15.808	26.7	22.750	31.2	32.382
8.8	4.984	13.3	7.435	17.8	10.951	22.3	15.938	26.8	22.932	31.3	32.633
8.9	5.029	13.4	7.500	17.9	11.044	22.4	16.070	26.9	23.115	31.4	32.886
9.0	5.075	13.5	7.566	18.0	11.138	22.5	16.202	27.0	23.300	31.5	33.141
9.1	5.121	13.6	7.632	18.1	11.233	22.6	16.335	27.1	23.485	31.6	33.397
9.2	5.167	13.7	7.699	18.2	11.328	22.7	16.470	27.2	23.673	31.7	33.656
9.3	5.214	13.8	7.766	18.3	11.424	22.8	16.605	27.3	23.861	31.8	33.916
9.4	5.261	13.9	7.834	18.4	11.521	22.9	16.742	27.4	24.054	31.9	34.178

Appendix 1.6

Flow rates (m^3 h^{-1})corresponding to the KROHNE flow meter scale

KROHNE flow meter, G21.12, AIII21- diagram No. 2

Scale	Flow m^3 h^{-1}	Scale	Flow m^3 h^{-1}	Scale	Flow m^3 h^{-1}	Scale	Flow m^3 h^{-1}
30	4.53	66	9.97	101	15.25	136	20.54
31	4.68	67	10.12	102	15.40	137	20.69
32	4.83	68	10.27	103	15.55	138	20.84
33	4.98	69	10.42	104	15.70	139	20.99
34	5.13	70	10.57	105	15.86	140	21.14
35	5.29	71	10.72	106	16.01	141	21.29
36	5.44	72	10.87	107	16.16	142	21.44
37	5.59	73	11.02	108	16.31	143	21.59
38	5.74	74	11.17	109	16.46	144	21.74
39	5.89	75	11.33	110	16.61	145	21.90
40	6.04	76	11.48	111	16.76	146	22.05
41	6.19	77	11.63	112	16.91	147	22.20
42	6.34	78	11.78	113	17.06	148	22.35
43	6.49	79	11.93	114	17.21	149	22.50
44	6.64	80	12.08	115	17.37	150	22.65
45	6.80	81	12.23	116	17.52	151	22.80
46	6.95	82	12.38	117	17.67	152	22.95
47	7.10	83	12.53	118	17.82	153	23.10
48	7.25	84	12.68	119	17.97	154	23.25
49	7.40	85	12.84	120	18.12	155	23.41
50	7.55	86	12.99	121	18.27	156	23.56
51	7.70	87	13.14	122	18.42	157	23.71
52	7.85	88	13.29	123	18.57	158	23.86
53	8.00	89	13.44	124	18.72	159	24.01
54	8.15	90	13.59	125	18.88	160	24.16
55	8.31	91	13.74	126	19.03	161	24.31
56	8.46	92	13.89	127	19.18	162	24.46
57	8.61	93	14.04	128	19.33	163	24.61
58	8.76	94	14.19	129	19.48	164	24.76
59	8.91	95	14.35	130	19.63	165	24.92
60	9.06	96	14.50	131	19.78	166	25.07
61	9.21	97	14.65	132	19.93	167	25.22
62	9.36	98	14.80	133	20.08	168	25.37
63	9.51	99	14.95	134	20.23	169	25.52
64	9.66	100	15.10	135	20.39	170	25.67
65	9.82						

Appendix 2.1

Calibration of gas meters:

Control of gas meters used in the sampling of particulate mercury (TPM-method) against a reference gas meter (Type: Ritter, TG 3, nr 13.733):

Date	*Gas meter, REMUS 3*	*Max flow ($l\ min^{-1}$)*	*Deviation (%)*
03.04.00	*Hg 1*	*7.10*	*5.41*
	Hg 2	*7.04*	*4.56*
	Hg 5	*7.17*	*6.47*
	Hg 10	*7.12*	*5.75*
07.09.00	*Hg 1*	*6.94*	*3.20*
	Hg 2	*6.84*	*1.72*
	Hg 5	*6.90*	*2.62*
	Hg 10	*6.91*	*2.75*

The sampling flow is corrected for the deviation according the equation:

$$\text{corrected value} = \frac{\text{measured value}}{1 + (X/100)}$$

X = deviation

Appendix 2.2

Detection limits – raw data:

Table A: Raw data for the determination of the detection limit for the TPM-trap method:

	Level 1	*Level 2*	*Level 3*
N	*10*	*10*	*10*
Result (pg Hg)	*0.90*	*1.79*	*0.32*
	0.54	*1.64*	*2.34*
	0.51	*1.02*	*0.10*
	0.50	*2.35*	*13.27*
	0.56	*1.87*	*2.96*
	0.69	*1.65*	*2.25*
	0.51	*2.46*	*8.91*
	0.60	*1.54*	*2.35*
	0.48	*1.59*	*4.00*
	0.58	*1.98*	*4.66*
SD (pg Hg)	*0.13*	*0.41*	*4.06*

Table B: Raw data for the determination of the detection limit for the glass fiber filter method:

	Level 1	*Level 2*	*Level 3*
N	*13*	*6*	*8*
Result (pg Hg)	*87.1*	*2.8*	*93.6*
	87.1	*2.8*	*119.4*
	64.4	*30.7*	*64.9*
	109.7	*160.3*	*96.5*
	64.4	*60.7*	*947.9*
	83.2	*81.9*	*268.3*
	43.8		*426.9*
	179.0		*834.7*
Result (pg Hg)	*60.7*		
	60.7		
	33.6		
	33.6		
	33.6		
SD (pg Hg)	*39.8*	*59.8*	*352.4*

Appendix 2.3

Raw data for the determination of accuracy and precision:

Table A: Raw data for the determination of accuracy and precision for the analytical set-up (TPM-trap method):

	Hg standard	detector respons	reported value
day	pg	area	pg
30-Sep	28	149884	25.3
30-Sep	28	149893	25.4
2-Oct	28	147135	25.0
2-Oct	28	152899	25.8
5-Oct	28	150660	25.0
5-Oct	28	143294	23.8
30-Sep	56	289767	49.2
30-Sep	56	291133	49.1
2-Oct	56	287128	48.5
2-Oct	56	297263	50.5
5-Oct	56	303306	50.2
5-Oct	56	272471	45.1
30-Sep	111	573404	96.7
30-Sep	111	569477	96.6
2-Oct	111	557685	94.7
2-Oct	111	575441	97.2
5-Oct	139	717730	119.2
5-Oct	139	673101	111.5
30-Sep	278	1417467	240.5
30-Sep	278	1402397	236.6
2-Oct	278	1396799	237.3
2-Oct	278	1426391	241.0
5-Oct	278	1442665	239.7
5-Oct	278	1373142	228.1
30-Sep	557	2853512	484.1
30-Sep	557	2805652	476.0
2-Oct	557	2780130	469.6
2-Oct	557	2839495	482.6
5-Oct	557	2933775	486.0
5-Oct	557	2732375	452.6

Table B: Raw data for the determination of intermediate precision for the analysis of Hg in solution (glass fiber filter method):

	Hg standard	detector respons
Day	(ng l^{-1})	(mm)
29-Nov	5	7.5
29-Nov	5	7
5-Dec	5	8
5-Dec	5	8.5
12-Dec	5	7.5
12-Dec	5	8
29-Nov	10	13
29-Nov	10	13
5-Dec	10	15
5-Dec	10	15
12-Dec	10	13.5
12-Dec	10	14.5
29-Nov	20	27
29-Nov	20	27.5
5-Dec	20	30
5-Dec	20	29
12-Dec	20	27.5
12-Dec	20	28
29-Nov	40	55
29-Nov	40	56
5-Dec	40	60.5
5-Dec	40	59
12-Dec	40	54.5
12-Dec	40	57
29-Nov	100	138.5
29-Nov	100	139
5-Dec	100	143
5-Dec	100	142
12-Dec	100	136
12-Dec	100	140.5

Table C: Raw data for the determination of accuracy and intermediate precision of the TPM-trap method.
Nist 1633 b is a standard reference material containing 0.141 ± 0.019 mg Hg kg^{-1}

date of analysis	**TPM-trap id**	**Nist 1633 b µg**	**measured conc. mg kg^{-1}**	**recovery %**
04.10.00	TPM 12	479	0.061	43.1
05.10.00	TPM 12	4512	0.054	38.4
06.10.00	TPM 13	1810	0.035	24.8
12.10.00	TPM 14	532	0.120	85.3
12.10.00	TPM 14	990	0.107	75.8
14.10.00	TPM 14	990	0.113	80.0
12.10.00	TPM 14	1508	0.112	79.3
14.10.00	TPM 14	1806	0.133	94.6
14.10.00	TPM 14	4921	0.120	85.3
15.10.00	TPM 14	1230	0.133	94.2
12.10.00	TPM 16	3278	0.043	30.8
04.10.00	TPM 2	905	0.136	96.4
04.10.00	TPM 2	1320	0.129	91.4
04.10.00	TPM 2	779	0.135	95.6
14.10.00	TPM 20	162	0.080	56.9
14.10.00	TPM 20	2555	0.141	99.9
14.10.00	TPM 20	3693	0.131	92.6
15.10.00	TPM 20	735	0.143	101.2
05.10.00	TPM 21	362	0.048	34.3
05.10.00	TPM 21	1161	0.025	18.0
05.10.00	TPM 21	3729	0.040	28.4
04.10.00	TPM 27	145	0.044	31.0
04.10.00	TPM 27	578	0.025	17.6
05.10.00	TPM 28	866	0.060	42.9
05.10.00	TPM 28	1211	0.121	85.5
05.10.00	TPM 28	4086	0.144	102.4
05.10.00	TPM 28	5039	0.135	95.6
05.10.00	TPM 28	5369	0.138	98.1
04.10.00	TPM 33	1093	0.022	15.4
04.10.00	TPM 33	1531	0.018	12.7
14.10.00	TPM 38	604	0.021	15.0
14.10.00	TPM 38	3845	0.027	19.5
12.10.00	TPM 39	1551	0.028	20.0
12.10.00	TPM 39	2075	0.024	17.1
12.10.00	TPM 39	2898	0.074	52.3
14.10.00	TPM 39	3948	0.058	41.4
12.10.00	TPM 39	8115	0.048	34.1
14.10.00	TPM 4	1376	0.042	29.5
14.10.00	TPM 4	1534	0.025	17.6
14.10.00	TPM 4	3928	0.029	20.3
15.10.00	TPM 4	2129	0.028	19.9
03.10.00	TPM 40	3389	0.023	16.0

Continues…

date of analysis	TPM-trap id	Nist 1633 b µg	measured conc. mg kg^{-1}	recovery %
15.10.00	TPM 41	1749	0.133	94.7
15.10.00	TPM 41	505	0.122	86.8
05.10.00	TPM 42	607	0.107	75.7
04.10.00	TPM 42	720	0.101	71.8
15.10.00	TPM 44	1230	0.095	67.6
15.10.00	TPM 44	802	0.087	61.8
03.10.00	TPM 47	4961	0.113	80.2
03.10.00	TPM 48	1981	0.128	90.8
06.10.00	TPM 48	1016	0.126	89.7
06.10.00	TPM 48	3420	0.129	91.6
04.10.00	TPM 48	845	0.100	70.6
15.10.00	TPM 49	1339	0.069	48.6
15.10.00	TPM 49	2482	0.072	51.0
12.10.00	TPM 6	2188	0.039	27.8
03.10.00	TPM 9	1661	0.129	91.8
03.10.00	TPM 9	3888	0.139	98.9

Table D: Raw data for the testing of recovery yields before (1.trial) and after (2.trial) a TPM is dismantled, cleaned and reconstructed. Nist 1633 b is a standard reference material containing 0.141 ± 0.019 mg Hg kg^{-1}

	date of analysis	TPM-trap id	Nist 1633 b µg	measured conc. mg kg^{-1}	recovery %
1. trial	04.10.00	TPM 2	779	0.135	95.6
	04.10.00	TPM 2	905	0.136	96.4
	04.10.00	TPM 2	1320	0.129	91.4
2. trial	14.10.00	TPM 2	1431	0.019	13.3
	14.10.00	TPM 2	2840	0.040	28.2
1. trial	12.10.00	TPM 6	2188	0.039	27.8
2. trial	15.10.00	TPM 6	1397	0.104	73.7

Table E: Raw data for the determination of accuracy and precision for the acid digestion method used for glass fiber filters:

detector respons mm	*Hg in 25 ml sample ng l^{-1}*	*blank correction ng l^{-1}*	*sample volume l*	*dilution factor*	*Nist 1633 b mg*	*measured value mg kg^{-1}*
52.5	*41.5*	*1.9*	*0.02625*	*1.6*	*13.467*	*0.123*
74.0	*58.2*	*1.9*	*0.02625*	*1.6*	*18.468*	*0.128*
56.5	*44.6*	*1.9*	*0.02625*	*1.6*	*11.309*	*0.159*
64.0	*48.0*	*1.9*	*0.02625*	*1.6*	*12.872*	*0.150*
57.5	*43.2*	*1.9*	*0.02625*	*1.6*	*12.512*	*0.139*
80.0	*59.7*	*1.9*	*0.02625*	*1.6*	*16.896*	*0.144*
72.5	*54.2*	*1.9*	*0.02625*	*1.6*	*15.588*	*0.141*

Appendix 3.1

Raw data from the Ny-Ålesund field study:

Table A: Field data and TPM concentrations at Ny-Ålesund from late April to late May. TPM was sampled on TPM-traps and detected on the GARDIS and TEKRAN systems.

start date year 2000	*sample id*	*sampling time (h)*	*flowrate l min^{-1}*	*volume m^3*	*TPM pg m^{-3}*	*arith mean pg m^{-3}*	*Analytical System*
29-Apr	*TPM 11*	*24*	*5.85*	*8.273*	0^c		*GARDIS*
	TPM 12		*3.87*	*5.229*	0^c	*0*	*GARDIS*
30-Apr	*TPM 6*	*22*	*6.05*	*8.133*	0^c		*GARDIS*
	TPM 5		*4.15*	*5.343*	0^c	*0*	*GARDIS*
1-May	*TPM 3*	*43*	*6.05*	*15.472*	*0.83*		*GARDIS*
	TPM 4		*3.94*	*9.644*	*1.32*	*1.08*	*GARDIS*
3-May	*TPM 10*	*23*	*5.53*	*7.665*	*1.49*		*GARDIS*
	TPM 7		*4.12*	*5.462*	*11.52*	*6.50*	*GARDIS*
4-May	*TPM 8*	*22*	*5.49*	*7.252*	*1.68*		*GARDIS*
	TPM 9		*4.05*	*5.118*	*2.71*	*2.20*	*GARDIS*
5-May	*TPM 14*	*25*	*5.54*	*8.211*	*687.20*		*TEKRAN*
	TPM 13		*4.02*	*5.700*	*55.93*	*371.57*	*TEKRAN*
6-May	*TPM 15*	*26*	*4.12*	*6.144*	*340.15*		*TEKRAN*
	TPM 16		*4.88*	*7.618*	*520.41*	*430.28*	*TEKRAN*
7-May	*TPM 18*	*22*	*5.49*	*7.100*	*878.58*		*TEKRAN*
	TPM 17		*4.06*	*5.025*	*754.48*	*816.53*	*TEKRAN*
8-May	*TPM 20*	*48*	*4.17*	*11.484*	*30.10*		*TEKRAN*
	TPM 22		*5.65*	*16.259*	*9.31*	*19.70*	*TEKRAN*
10-May	*TPM 24*	*27*	*5.48*	*8.750*	*139.90*		*TEKRAN*
	TPM 23		*4.26*	*6.504*	*28.69*	*84.29*	*TEKRAN*
11-May	*TPM 26*	*23*	*5.44*	*7.526*	*86.38*		*TEKRAN*
	TPM 25		*4.07*	*5.382*	*78.28*	*82.33*	*TEKRAN*
12-May	*TPM 29*	*45*	*5.73*	*15.552*	*31.04*		*TEKRAN*
	TPM 28		*4.09*	*10.471*	*35.42*	*33.23*	*TEKRAN*
14-May	*TPM 31*	*32*	*3.94*	*7.202*	*61.10*		*TEKRAN*
	TPM 32		*2.33*	*4.453*	*258.80*	*159.95*	*TEKRAN*
15-May	*TPM 34*	*70*	*3.95*	*15.803*	*77.52*		*TEKRAN*
	TPM 36		*5.89*	*24.617*	*14.30*	*45.91*	*TEKRAN*
18-May	*TPM 38*	*40*	*4.01*	*9.045*	*16.64*		*TEKRAN*
	TPM 37		*3.96*	*9.082*	*41.00*		*TEKRAN*
	TPM 39		*5.37*	*12.896*	*5.83*	*21.16*	*TEKRAN*
20-May	*TPM 7*	*48*	*5.49*	*15.823*	*5.21*		*TEKRAN*
	TPM 3		*3.91*	*10.790*	*3.79*		*TEKRAN*
	TPM 4		*3.96*	*10.708*	*8.51*	*5.84*	*TEKRAN*

c: value is lower than the background of the analytical system

Table B: Blank values obtained by analysis of operational blanks (TPM-traps) from the Ny-Ålesund fieldwork.

blank no.	*date*	*pg Hg*	*Analytical system*
Blank 1	*3-May*	*19.4*	*GARDIS*
Blank 2	*3-May*	*1185.1*	*TEKRAN*
Blank 3	*7-May*	*2959.7*	*TEKRAN*
Blank 4	*8-May*	*474.1*	*TEKRAN*
Blank 5	*11-May*	*5990.6*	*TEKRAN*
Blank 6	*12-May*	*296.6*	*TEKRAN*
Blank 7	*14-May*	*2869.2*	*TEKRAN*
Blank 8	*15-May*	*6632.2*	*TEKRAN*
Blank 9	*18-May*	*1459.6*	*TEKRAN*
Blank 10	*20-ay*	*69.0*	*TEKRAN*
Blank 11	*22- May*	*215.3*	*TEKRAN*
mean		*2015.5*	
SD_B		*2368.1*	

Table C: Field data and TPM concentrations at Ny-Ålesund from late February to September. TPM was sampled on glass fiber filters and detected on the MERLIN system after HNO$_3$-digestion.

Sample Id	*start date Year 2000*	*sampling time (h)*	*flowrate l min^{-1}*	*Volume m^3*	*TPM pg m^{-3}*	*arith mean pg m^{-3}*
	25-Feb	*119*	*24.10*	*2873.9*	*0.45*	*0.45*
	3-Mar	*120*	*23.35*	*2805.9*	*5.75*	*5.75*
	10-Mar	*120*	*5.82*	*696.8*	*0.70**	*0.70*
	24-Mar	*120*	*5.82*	*696.8*	*4.40*	*4.40*
	31-Mar	*120*	*6.04*	*723.0*	*4.95*	*4.95*
	7-Apr	*72*	*3.02*	*217.4*	*10.46*	*10.46*
1	*29-Apr*	*25*	*6.04*	*161.6*	*8.33*	
2			*5.42*	*152.1*	*3.29**	*5.81*
3	*30-Apr*	*21*	*5.66*	*116.9*	*3.14**	
4			*6.72*	*138.7*	*10.02*	*6.58*
5	*1-May*	*43*	*6.12*	*260.6*	*12.56*	*12.56*
6	*3-May*	*24*	*6.04*	*145.1*	*31.00*	
7			*5.66*	*135.9*	*31.08*	*31.04*
8	*4-May*	*23*	*5.89*	*132.5*	*25.73*	
9			*6.57*	*147.1*	*28.14*	*26.93*
10	*5-May*	*25*	*5.89*	*146.3*	*20.68*	
11			*6.42*	*159.3*	*23.54*	*22.11*
12	*8-May*	*46*	*6.04*	*276.1*	*12.59*	
13			*5.97*	*272.7*	*18.90*	*15.75*
14	*12-May*	*47*	*5.74*	*267.6*	*30.24*	
15			*5.97*	*278.1*	*24.99*	*27.61*
16	*14-May*	*32*	*6.12*	*194.6*	*49.04*	
17			*6.04*	*192.2*	*44.52*	*46.78*
18	*15-May*	*38*	*5.74*	*217.4*	*19.02*	
19			*5.97*	*225.9*	*16.00*	*17.51*
20	*19-May*	*70*	*6.04*	*422.3*	*1.58**	
21			*5.89*	*411.8*	*5.42*	*3.50*
22	*22-May*	*48*	*6.04*	*289.9*	*0**^{a}	
23			*6.04*	*289.9*	*0**^{a}	*0*^{a}
	26-May	*72*	*5.79*	*417.1*	*0.45**	*0.45*
	9-Jun	*120*	*6.04*	*723.4*	*1.35**	*1.35*
	23-Jun	*72*	*6.04*	*436.1*	*2.02**	*2.02*
	30-Jun	*120*	*6.12*	*730.9*	*1.46**	*1.46*
	7-Jul	*120*	*6.04*	*721.9*	*1.31**	*1.31*
	14-Jul	*120*	*6.04*	*723.9*	*2.81*	*2.81*
	21-Jul	*119*	*6.12*	*730.6*	*2.04*	*2.04*
	28-Jul	*120*	*6.04*	*722.8*	*0.33**	*0.33*
	4-Aug	*120*	*6.04*	*722.3*	*1.73**	*1.73*
	11-Aug	*120*	*6.34*	*761.9*	*1.32**	*1.32*
	18-Aug	*119*	*6.04*	*721.4*	*1.19**	*1.19*
	25-Aug	*120*	*6.19*	*745.4*	*0.74**	*0.74*
	1-Sep	*119*	*6.27*	*746.7*	*0.44**	*0.44*
	8-Sep	*119*	*6.34*	*757.3*	*0.65**	*0.65*
	15-Sep	*120*	*6.04*	*725.3*	*0.19**	*0.19*
	22-Sep	*120*	*6.50*	*776.2*	*0.15**	*0.15*

[a] Mean blank value exceeds sample value

*Value is below detection limit

Table D: Blank values obtained by analysis of operational blanks (glass fiber filters) from the Ny-Ålesund fieldwork

blank no.	*date*	*TPM pg Hg*
blank 1	*3- May*	*947.9*
blank 2	*10- May*	*268.3*
blank 3	*16- May*	*426.9*
blank 4	*20-May*	*834.7*
blank 5	*1-Aug*	*64.9*
blank 6	*1- Sep*	*96.5*
blank 7	*22- Sep*	*119.4*
mean (1-4)		*619.5*
SD_B *(1-4)*		*323.8*
mean (5-7)		*93.6*
SD_B *(5-7)*		*27.3*

Appendix 3.2

Raw data from the Mediterranean Sea field study

Table A: TPM-concentrations at the Mediterranean measured during 29th of July to 9th of August

sample Id	*start date year 2000*	*sampling time (h)*	*flow rate* $l\ min^{-1}$	*volume* m^3	*TPM* $pg\ m^{-3}$	*TPM mean* $pg\ m^{-3}$	*analytical system*
TPM 47	*29-Jul*	*23*	*4.2*	*5.6*	*0*[a]		*GARDIS*
TPM 45			*5.6*	*7.7*	*0*[a]	*0*[a]	*GARDIS*
TPM 9	*30-Jul*	*24*	*4.1*	*5.6*	*23.98*		*ITALY*[c]
TPM 11			*5.0*	*7.1*	*-*	*23.98*	*ITALY*[c]
IT. 29	*31-Jul*	*25*	*2.7*	*3.8*	*-*		*ITALY*[c]
IT. 15			*3.3*	*5.0*	*1.58**	*1.58*	*GARDIS*
TPM 8	*1-Aug*	*21*	*4.9*	*5.9*	*26.21*		*ITALY*[c]
TPM 44			*5.3*	*6.7*	*26.30*	*26.25*	*ITALY*[c]
TPM 42	*2-Aug*	*10*	*10.2*	*5.9*	*19.76*		*GARDIS*
TPM 47			*11.9*	*7.2*	*-*	*19.76*	*GARDIS*
TPM 51	*3-Aug*	*35*	*3.5*	*7.3*	*1.98**		*TEKRAN*
TPM 46			*2.6*	*5.3*	*9.96*	*5.97*	*IVL*[d]
TPM 12	*4-Aug*	*3*	*6.2*	*1.1*	*0**[a]		*GARDIS*
TPM 48			*5.1*	*0.9*	*101.33*[b]	*0*	*GARDIS*
TPM 11	*5-Aug*	*27*	*4.6*	*7.1*	*0**[a]		*TEKRAN*
TPM 50			*5.2*	*8.4*	*10.38*	*5.19*	*TEKRAN*
TPM 45	*6-Aug*	*23*	*5.4*	*7.3*	*10.45*		*TEKRAN*
TPM 8			*5.1*	*6.6*	*9.42*	*9.94*	*IVL*[d]
TPM 48	*7-Aug*	*24*	*4.2*	*5.9*	*16.20*		*TEKRAN*
TPM 44			*5.2*	*7.6*	*6.25*	*11.23*	*TEKRAN*
TPM 43	*8-Aug*	*19*	*5.7*	*6.5*	*18.94*		*TEKRAN*
TPM 9			*4.7*	*5.1*	*28.17*	*23.56*	*TEKRAN*

a Mean blank value exceeds sample value

b Contaminated

c Analysed at the Italian system (CNR-IIA)

d Analysed at IVL Swedish Environmental Research Institute by Invar Wangberg

\- Failure in the analytical system

* Value is below detection limit

Table B: Blank values obtained by analysis of operational blanks from the Mediterranean fieldwork

Blank no.	*date*	*pg Hg*	*Analytical system*
Blank 1	*29-Jul*	*5.44*	*GARDIS*
Blank 2	*30-Jul*	*17.94*	*ITALY*[c]
Blank 3	*1-Aug*	*18.08*	*ITALY*[c]
Blank 4	*3-Aug*	*6.70*	*GARDIS*
Blank 5	*3-Aug*	*3.57*	*IVL*[d]
Blank 6	*5-Aug*	*7.03*	*TEKRAN*
Blank 7	*6-Aug*	*12.79*	*TEKRAN*
Blank 8	*7-Aug*	*29.43*	*TEKRAN*
Mean		*12.62*	
SD_B		*8.79*	

c Analysed at the Italian system (CNR-IIA)
d Analysed at IVL Swedish Environmental Research Institute by Invar Wangberg

Appendix 3.3

Raw data from the Kjeller field study

Table A: Field data and TPM concentrations at Kjeller. TPM was samples on TPM-traps and detected on the TEKRAN system.

Date year 2000	*sample id*	*sampling time (h)*	*flow rate l^{-1} min*	*volume m^3*	*TPM pg m^3*
20-Sept	TPM 17	26	4.0	6.3	47.36
	TPM 21		5.5	8.5	39.48
	TPM 27		6.6	10.3	17.93
	TPM 33		6.0	9.4	19.34
25- Sept	TPM 32	23	4.0	5.6	49.96
	TPM 38		5.7	8.0	40.36
	TPM 42		5.3	7.4	5.52
	TPM 49		5.7	8.0	5.77
26- Sept	TPM 31	24	5.5	7.8	100.03
	TPM 33		4.2	6.0	99.15
	TPM 4		5.4	7.6	88.27
	TPM 3		5.6	8.0	90.57
27- Sept	TPM 15	23	4.2	5.8	114.13
	TPM 16		6.3	8.7	85.32
	TPM 24		5.2	7.2	94.24
	TPM 26		5.6	7.7	103.80
28- Sept	TPM 39	25	4.7	6.9	73.67
	TPM 5		5.5	8.1	95.44
	TPM 6		5.8	8.6	6.84
	TPM 7		4.6	6.8	93.20
29- Sept	TPM 19	20	5.9	7.1	179.97
	TPM 27		4.4	5.3	31.20
	TPM 33		6.1	7.4	37.44
	TPM 42		5.6	6.8	69.66
4-Oct	TPM 20	23	4.1	5.5	5.39
	TPM 22		5.8	8.0	24.16
	TPM 28		5.6	7.7	3.41
5- Oct	TPM 37	23	4.1	5.8	8.97
	TPM 41		5.7	8.0	4.69
	TPM 50		5.5	7.7	3.61
10- Oct	TPM 12	23	3.8	5.4	4.82
	TPM 37		6.0	8.3	22.02
	TPM 43		5.2	7.3	36.42
11- Oct	TPM 0	22	4.3	5.8	60.94
	TPM 15		5.3	7.2	46.72
	TPM 31		5.4	7.3	33.02
12- Oct	TPM 49	21	4.4	5.4	43.60
	TPM 44		5.1	6.3	46.82
	TPM 41		6.3	7.8	4.79

Table B: Blank values obtained by analysis of operational blanks (TPM-traps) from the fieldwork at Kjeller.

Date	blank no.	pg Hg
25.09.00	1	0.32
27.09.00	2	2.34
28.09.00	3	0.10
30.09.00	4	13.27
30.09.00	5	2.96
02.10.00	6	2.25
06.10.00	7	8.91
11.10.00	8	2.35
13.10.00	9	4.00
15.10.00	10	4.66
Mean		4.12
SD_B		4.06

Table C: Field data and TPM concentrations at Kjeller. TPM was sampled on glass fiber filters and detected on the MERLIN system after HNO_3-digestion.

date	Sample Id	sampling time (h)	flow rate m^3 h^{-1}	volume m^3	TPM pg m^3	arith mean pg m^3
27.09.00	A	23	6.04	139.3	11.54	
	B	23	6.04	139.3	11.64	11.59
28.09.00	C	25	5.66	139.5	11.26	
	D	25	5.97	147.0	9.07*	10.17
04.10.00	I	23	5.51	125.7	15.98	
	J	23	5.36	122.3	13.13	14.55
05.10.00	L	23	5.74	133.9	10.43	
	M	23	5.82	135.7	11.47	10.95
10.10.00	N	23	5.44	126.7	9.42*	
	O	23	5.51	128.5	8.05*	8.73
11.10.00	P	22	5.89	131.5	9.42*	
	Q	22	5.66	126.4	10.52*	9.97
12.10.00	R	21	6.04	123.9	9.06*	
	S	21	6.04	123.9	9.08*	9.07
05.10.00	blank				94.48 pg	

* Value is below detection limit

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ABSTRACT
The goal has been to implement the use of a custome-made quartz trap for measuring total particulate mercury (TPM) in the atmosphere. This new method is an improvement compared to conventional methods, as a minimum of handling steps is required between sampling and analysis.

NORWEGIAN TITLE
Utvikling av metode for prøvetaking og bestemmelse av partikulært kvikksølv i atmosfæren.

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