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Development of a method for sampling and quantifying Gaseous Divalent Mercury (GDM)

Candidata Scientiarum

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Anne-Kari Valdal

Contents

Summary

The call for methods for speciation of the atmospheric mercury species has grown over the last two decades, as their wide variety of properties has been discovered. A special interest has been taken in the divalent mercury species, which are highly reactive and water soluble, leading to an increased deposition rate to terrestrial surfaces.

A development of a method for sampling and quantifying gaseous divalent mercury (GDM), has been done. The method is based on sampling of mercury by adsorption on KCl coated annular denuders. The samples are introduced to the analyser by thermal desorption of the denuders. Gaseous divalent mercury is thermally reduced to elemental mercury, and quantification is completed by atomic absorption spectroscopy (AAS).

A system for sampling GDM from ambient air, and another for introducing the sample into an analyser, have been built. Through testing of the systems in the laboratory, and through field studies, the need for improvements of the initial systems was discovered. Several modifications has been conducted to procedures and parts, in order to optimise the systems. Less time consuming procedures, higher sampling efficiency and more stable and reliable systems has been obtained.

Performing tests in the laboratory, a limit of detection for introduction and analysis system of 0.6 pg, was attained. The calculations were based on repeated measurements of the mercury background from these systems. By analysing several denuder sample blanks, a limit of detection of 2.1 pg (ca 1 pg/m^3) for the whole sampling and analysis process was acquired.

Performing the same tests at the field laboratory at Svalbard, the corresponding limits obtained were 1.2 pg and 8.4 pg (> 4 pg/m^3) respectively. In the same laboratory an experiment was performed were the AAS based analyser was exchanged with an AFS (atomic fluorescence spectroscopy) based. The obtained limits of detection for introduction and analysis system were then 0.42 pg.

The method has been applied for GDM measurements during two field studies at Ny-Ålesund, Svalbard. The mission of the studies was to investigate the theory of GDM formation during elemental mercury depletion episodes in Arctic regions. The episodes, and the sampling campaigns, took place in April and May, shortly after polar sunrise. The first study (2000) showed a negative correlation of about 0.8 between measured elemental mercury concentrations and GDM concentrations. During spring of 2001, few depletion episodes were observed, and the correlation was not calculated. Further results from the field studies are reported.

A sampling campaign has also been performed close to industrial sources over the Mediterranean Sea, and the results are reported.

Development of a method for sampling and quantifying Gaseous Divalent Mercury (GDM)

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1 Introduction

Mercury has had a wide variety of uses to man for thousands of years. Only a few hundred years ago, the first descriptions of mercury's toxic effects appeared in literature. It is now well known that this heavy metal can cause severe damages to humans, as well as animals and plants.

One of mercury's many special properties is its high vapour pressure. Unlike any other heavy metal, the mercury can be vaporised to ambient air at low temperatures, and it exists in the atmosphere predominantly in the elemental form. The elemental form is fairly unreactive. The mercury can travel long distances in the atmosphere before it is deposited back to earth. Mercury is thus a global pollutant, causing environmental problems far away from its sources.

A range of both natural and anthropogenic sources contributes to the overall emission of mercury. Recent estimates suggest that twice as much mercury is released from manmade sources, as from the natural ones[1]. The estimates suffer, however, from the lack of reliable data. A major challenge in the future will therefore be to quantify the emanations, and consequently develop proper methods to reduce them.

Today it is well known that the different mercury species have substantial dissimilarities in their toxicity. Recent research has discovered very different chemical and physical characteristics that affect mercury's transportation, deposition and influences on ecosystems. Special interest has been taken in the divalent oxidised forms, Hg(II), and their unique properties. While the elemental mercury, Hg°, can travel very long distances in the air, up to thousands of kilometres, the gaseous divalent mercury, GDM, will be removed in the vicinity of a few tens to a few hundreds of kilometres. Mercury associated with particulate matter will be deposited at intermediate distances[2].

Despite the well-accepted fact that Hg° constitutes 95-99% of the total mercury amount in air, indications are that the Hg(II) species may control the overall deposition of mercury to the terrestrial systems. This is due to the reactivity and high water solubility of the species. They are easily deposited back to the earth's ecosystems by both wet and dry deposition[3]. Speciation of atmospheric mercury is crucial for predicting deposition and understanding the biochemical cycle of mercury. A regional dispersion model, developed and applied by the German Federal Environmental Agency, showed a significant effect of the presence of GDM on the deposition pattern in Europe. A total lack of validated measurement data for GDM made it impossible though, to evaluate the model performance[4]. The limited investigations can be a result of the extremely low concentrations of Hg(II) species in ambient air. A few research groups from different parts of the world are now trying to develop suitable methods for sampling and quantifying these species.

In some areas speciation of mercury are of special interest. Elemental mercury is dominant in the reducing conditions of a gasification flue gas, but the decreasing temperature in a combustion flue gas will make Hg° react to form Hg(II) compounds. It is thought that more than 50% of the Hg° in coal combustion flue gases reacts in this way. The increased amount of the reactive Hg(II) species will have a great impact on the local deposition of mercury[5].

Recently, several depletion episodes of elemental mercury, shortly after polar sunrise, have been observed in the Arctic regions. Similar episodes are well known for tropospheric ozone in the same areas. It is proposed that the elemental mercury is oxidised during these episodes, forming reactive Hg(II) species like GDM and TPM (total particulate mercury). These forms are much more available to biota than Hg°, and may cause a considerable deposition flux of mercury during the vulnerable time of preparing for peak summertime activity[6].

The aim of this study is to develop a method for sampling and quantifying gaseous divalent mercury, GDM, and to test the method in target areas close to industrial sources and in the arctic region.

1.1 History – a short review

Man has known mercury, and some of its very special properties, for centuries and maybe for thousands of years. Some sources[7] claims that the medicinal use of mercury can be traced back further than 3000 years. There are some indications that calomel ($HgCl_2$) was used to cure venereal diseases and that cinnabar (HgS) was used as writing ink in China 2000 BC. In India, mercurials were known as medicines at least from 500 BC[8].

The chemical symbol Hg derives from the term hydrargyrum (Greek water (ηψδορ), and silver (αργψροσ)) used by the Romans. By eastern and western alchemists all the other metals were assigned a strict gender while mercury was thought to be hermaphroditic. Apparently they also thought mercury to be in spiritual correspondence with the planet Mercury[9]. Mercury has had a widespread use as an extractor in amalgamation of precious metals. For this purpose the Spanish took large amounts of mercury to "The New World" and brought silver back home. In several cultures in "The New World", among them the Mayans, mercury also had ritual importance, and was used in the struggle against evil forces[10].

In 1533, Paracelsus was the first to describe mercury poisoning among workers in mercury mines as an occupational disease. The amounts of reports on mercury poisoning among workers of different occupations increased rapidly during the 18th and 19th century. Parallel to this, mercury was introduced for an increasing number of purposes such as antiseptic, diuretic and chemotherapeutic[7].

For centuries scientists did not distinguish between the various chemical forms of mercury, despite all the differences in properties. In 1852 Edward Frankland reported the first organo-mercury compound (CH_3HgI). Three of his co-workers died as a consequence of inhaling the poisonous compounds during these findings, and very little research was carried out on the organo-mercurials until the beginning of the next century. Organo-mercurials are now known to be highly toxic. They attack the nervous system by binding to the sulphydryl groups in the proteins, as well as induce disturbance in foetal development[9].

The environmental problems caused by mercury were first discovered in the 1950s. Large amounts of mercury were released into air and water through the use as a seed disinfectant and fungicide. Also the chlor-alkali industry was responsible for large emissions of mercury. In the 60s several bird species were threatened by extinction because of mercury poisoning, and elevated amounts of mercury were measured in fish living in contaminated lakes[11].

Two very tragic pollution events put the focus on environmental mercury as a danger to man. In Minamata, Japan, a major manufacturer of organic chemicals released large amounts of mercury into the bay area during the late 50s. The mercury was biomagnified in fish and ingested by the poor local fishing people. The mercury poisoning, known as "Minamata disease", caused more than 900 deaths. In 1972 in Iraq, several hundred people died from mercury poisoning after eating bread prepared from wheat seed treated with a mercury fungicide[9].

Several steps were taken world wide to reduce the releasing of mercury into the environment. Mercury as a seed disinfectant was banned. In the 70s many positive results were seen and the mercury problem was thought to be solved. Nevertheless, in the 80s elevated levels of mercury were recorded in several lakes situated far away from any emission source. The “new” problem was connected to widespread air pollution and long transportation. It was said that “The mercury problem has changed from a situation which could be described as local and acute, resulting from point source emissions, to a situation which is regional and chronic”[12].

1.2 The toxic effects of mercury

1.2.1 The effects on plants and animals. The food chain.

Mercury is one of the most venomous environmental toxins. The Norwegian environmental authorities have listed mercury on the top priority list for the investigation of especially toxic and dangerous pollutants. As mentioned above, the different mercury species possess various properties. All mercurials are toxic, the organo-mercury species being by far the most toxic compounds. Even though a major part of the mercury introduced to the environment is in metallic form, micro-organisms will, as a part of their defence mechanism, biomethylate the mercury into its organo-metallic form and thus make it both more available to the plants and animals, and more toxic[13].

Mercurials are, especially after conversion to the organo-metallic form, both bactericides and fungicides. They will also inhibit a variety of intracellular enzymes[7]. Generally, mercury will reduce the uptake of potassium and phosphate and decrease the translocation in plants. Exposure to large concentrations may cause severe root damage and will affect water and nutrient uptake. In turn this will affect the photosynthesis and lead to reduced growth[13].

In animals mercury poisoning can lead to a wide range of physiological and biochemical abnormalities. Among the most serious effects are reduced reproduction by inhibition of eggs and sperm together with severe foetal injuries, and even death may occur. Other effects are lessened food consumption, leading to reduced growth, decreased respiratory rate, distress, hyperactivity, blindness and lack of movement[13].

Besides the direct damage mercury pollution will bring upon the environment, the accumulation of the toxin in the food chain is a serious threat to humans. The mercury concentration will increase in the successive levels of the food web, from the primary producers to the terminal carnivorous consumers. For man, placed on the top of the food chain, this bio magnification will be of crucial importance when it comes to total exposure of mercury. The bioaccumulation process of mercury can also be affected by other anthropogenic pollution problems. Increased acidification of lakes may give a new type of food chain and such amplify accumulation in fish. The bio-methylation of mercury in microorganisms will also be accelerated in an acidic environment[14].

1.2.2 Health effects on humans

Humans can be exposed to the different mercury species in various ways. Exposure to the skin can be both by direct contact, or caused by high concentrations in ambient air. Intake of mercurials can be through inhalation, orally or by injections. The main source of organic mercury is undoubtedly nutrition. At the top of the food chain the bio magnification of mercury becomes noticeable[11]. Effects from elemental and inorganic mercury are most commonly seen among workers exposed occupationally. Urban et al. (1996)[15], describes the results of examinations of workers exposed to about 0.25 mg/m^3 mercury over an average of nine years. The examinations showed that 80% of the workers suffered from erythrism, 51% had abnormal VEPs (Visually Evoked Potentials) and 25% were suffering from tremors in their fingers.

The gravity of the effects from mercury exposure depends both on their amount and form. The exact lethal doses for humans are not very well known. The human LD_{10} (lethal dose for 10 % of a population) for elementary mercury is thought to be about 1430 mg/kg and it is believed that this species is converted to ionic forms before it gives a toxic effect. Mercury salts are irritants and corrosive to the skin. Divalent compounds are more toxic than the monovalent ones. The lowest observed lethal dose for $HgCl_2$ is an LD_{10} of 29 mg/kg. The acute toxic dose for the organo-mercurial MeHgCl is an oral LD_{10} of 5 mg/kg[7].

Mercury poisoning has a wide variety of symptoms, ranging from drowsiness, headache and coughing, to death. Typical indications of acute poisoning are coughing blood, heavy breathing and reduced lung capacity. $HgCl_2$ can cause kidney failure. Very large doses will lead to death. Chronic poisoning is characterised by different symptoms. Tremors, co-ordination failure, reduced vision and concentration problems are typical signs[8]. In general, some of the most severe consequences of mercury poisoning are emotional and psychological disturbances, impairment of immune response, chromosomal aberrations and serious damage to the nervous system. Observations show that mercury accumulates in the foetus. This can initiate uneventful deliveries, abnormalities on the foetus, neurological injury as well as physical and mental retardation[7].

1.3 Physical and chemical properties[2,7,16]

The atomic number of mercury is 80, its atomic weight is 200.59, and the chemical symbol is Hg. It is a transition metal in the IIB group together with zinc and cadmium, and has a closed shell electronic configuration ($5d^{10}6s^2$). While zinc and cadmium are electropositive, mercury is relatively inert. There are seven stable isotopes of mercury, and Hg gives a characteristic isotopic pattern in spectrometric investigations. Four radioactive isotopes also exist, among them the ^{197}Hg with a half-life of 64.1 hours, and ^{203}Hg with a half-life of 46.6 days. These are valuable isotopes in instrumental neutron activation analysis because of their emission of γ-rays. Other properties are constant volume of expansion over the entire temperature range of its liquid state, high surface tension, low electrical resistance and a specific gravity of 13.55 g/cm^3. Elemental mercury, Hg°, is a silver-white liquid at 25°C, and is the only metal that is a liquid at STP. Mercury has three different oxidation states, 0, +1 and +2. Hg° (oxidation state 0), has a high vapour pressure, and is the predominant form in the atmospheric environment. The oxidation state +1 is in form of the highly unstable dimer Hg_2^{2+} and might be non-existent in the atmosphere. Hg^{2+} acts as a soft acid and readily forms complexes with ligands such as OH^-, Cl^-, Br^-, I, SO_3^{2-} and CN^-. In nature mercury is mainly found as a sulphide (cinnabar), and elemental Hg is produced by heating these mercury ores to liberate the Hg° vapour before it is condensed to liquid Hg. Hg combines with noble metals (Au, Ag, Pt, and Pd) to form amalgams and was for many years an important extractor of gold. In the atmosphere Hg can equilibrate among gaseous, aqueous and solid phases.

1.4 Mercury as a global pollutant

Following the Minamata disaster in the 1960s, disposal of mercury-containing wastes directly into rivers and lakes was virtually eliminated. Nevertheless, elevated and increasing concentrations of mercury were found in fish from lakes far away from any possible sources. This led to the belief that atmospheric mercury depositions were responsible for the contaminations. Today the atmospheric pathway of the mercury cycle is known to be the primary source of mercury threatening remote lake areas[17].

Mercury, as a metal, has many unique properties. It is highly volatile and exists in the atmosphere primarily in the gaseous state. Mercury compounds are easily reduced to the elemental form, Hg°, which is relatively unreactive and not very soluble in water. These special properties give mercury an atmospheric residence time of about one year. Other metals are attached to particles and will only persist in the atmosphere for days or at most a few weeks. As a result, mercury can be transported thousands of kilometres before removal, and thus act as a global pollutant[2].

Mercury may be deposited to environmental surfaces both by wet and dry deposition, but the dominant elemental specie is transported back to earth principally by dry deposition. Once deposited to surfaces mercury is, due to its high volatility, readily re-emitted to air[18]. In that way mercury can travel long distances in several leaps. High levels of mercury contamination have been observed in the Arctic, and it is believed that the cold Arctic climate may favour a final deposition there[19].

1.5 Atmospheric mercury

1.5.1 Emissions

1.5.1.1 Sources

Numeral natural and anthropogenic sources release and re-emit mercury into the air. Until the middle of the 1980s the anthropogenic sources were thought to be minor, or even insignificant compared to the emissions from natural sources[20]. A combination of measurements, calculations and modelling led to the understanding that manmade emission sources could be much more significant than earlier assumed, maybe even a larger contributor to atmospheric mercury than the natural ones. In 1988 Nriagu and Pacyna estimated world wide anthropogenic emissions for the year 1983 to be in the range 910-6200 tons, while the natural emissions were estimated to about 3000 tons[21]. More recent studies estimates natural emissions to be 2000 tons a year[22], and anthropogenic to be 4000 tons a year[1]. Natural emission estimates suffer especially under the lack of sufficient data today. A major problem is to separate the fluxes of mercury from natural sources from the re-emitted mercury originally released from anthropogenic sources[2].

Major natural sources of atmospheric mercury are earth's mantle/crustal material, surficial soils, water bodies and vegetation. Weld fires and volcanoes also contribute to the release of mercury. Prior to the 1970s chlor-alkali plants released the greater part of manmade atmospheric mercury. The implementations of control and guidelines have radically reduced the emission from this and some of the other major contributors. Pacyna et al.[23] states, in a report from 2001, that the European anthropogenic emissions were decreased by 45% from 1990 to 1995. Most of the reduction was due to lessened emissions from chlor-alkali industry, while emissions from coal combustion had not changed significantly. Today the most important anthropogenic sources are coal combustion and waste incineration. Others are metal smelting, refining and manufacturing. An increasing amount of mercury is also released from crematoriums. This is a result of the use of amalgam in dental health care for decades[2,16].

1.5.1.2 Speciation of sources

Very few investigations have been made on the speciation of natural emissions. The natural sources are thought to release mostly elemental mercury, Hg°, but Hg bound to particulate matter has been observed in emission from volcanoes. Emission of volatile inorganic compounds and dimethylated mercury cannot be ruled out, but dimethylated mercury is expected to be relatively short lived due to rapid oxidation by hydroxyl radicals[24].

Particularly three different mercury species emitted from anthropogenic sources, are considered important in the overall cycling of mercury. The relatively inert dominant elemental form, Hg°, can be transported over very long distances making the emission a global problem. The highly reactive gaseous Hg(II) forms will contribute heavily to the local deposition, and the mercury associated with particulate matter will be deposited at intermediate distances depending on the size of the particles. Also methylated mercury species have been shown to be present in air[25], but he sources of these forms are not well known.

The concentration of total gaseous mercury in ambient air can exhibit strong diurnal cycles under certain meteorological conditions, especially in layers of air close to the earth's surface[26]. Also seasonal variations have been observed on several occasions, but seem to differ from place to place. Generally the variations appear to be vastly dependent on the proximity or absence of strong Hg-emitting point- or area sources.

1.5.2 The cycling of atmospheric mercury

The mercury released from natural and anthropogenic sources can take a number of different pathways in the environment. The specific pathway taken by a given species depends both on its own physical and chemical characteristics as well as the environmental and meteorological conditions it experiences in the atmosphere. Inorganic mercury species released into the atmosphere might be converted into highly toxic methyl mercury species by natural occurring biological processes. A special characteristic of mercury compared to other heavy metals in the atmosphere, is the ability to recycle to the air once deposited to terrestrial surfaces. Another is that mercury exists predominantly in the vapour phase in air, while other metals usually exists in the solid phase. The long residence time in the atmosphere makes mercury a much more "far reaching" pollutant than other metals[2].

1.5.2.1 Reactions and transformations in the atmosphere

A very large part of the Hg-reactions in the atmosphere is thought to take place in aqueous aerosols, in fog droplets in clouds. In 1995 Pleijel and Munthe[27], performed a series of experiments concerning possible aqueous transformations in the atmosphere. They used the CAM-model (Chemistry of Atmospheric Mercury) to test the impact of different parameters on the reactions. This model was described by Pleijel and Munthe in 1994[28]. Figure 1 shows most of the important transformations included in the model.

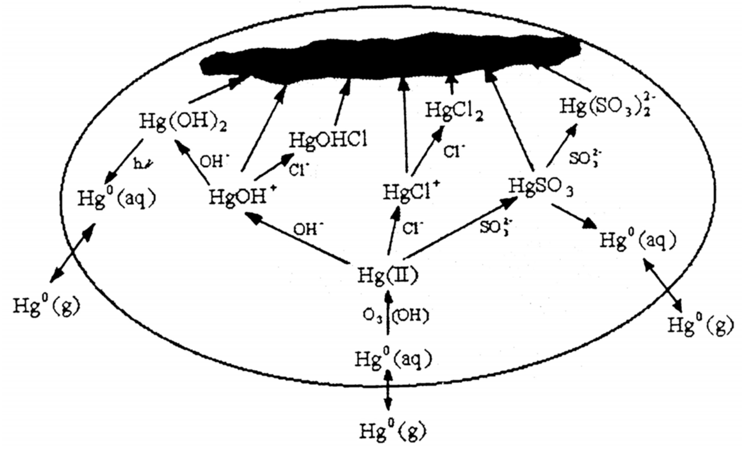

Figure 1: Mercury transformations occurring in a fog droplet. Elemental mercury from emission sources enters the droplet until equilibrium is established. Aqueous oxidation of Hg° transfers Hg from the air to the droplet. Reduction of Hg(II) will act in the reverse direction. Some mercury complexes adsorbs to particles within the droplet (upper part of figure)[27].

An important reaction is the oxidation of Hg° to Hg(II) by ozone. Hg(II) can then be present as $HgSO_3$, $Hg(SO_3)_2^{2-}$, $HgCl^+$, $HgCl_2$, $HgOH^+$, $Hg(OH)_2$ or HgOHCl. Hg(II) can be reduced back to Hg°, released from the fog droplets and return to the gas phase. Hg(II) can also be adsorbed onto particles in the droplets. The dominant specie in the droplet is the particulate mercury, while the most common dissolved ones are $HgCl_2$ and HgOHCl. The figure below shows the test results of the effects on Hg(II) concentration, when changing different parameters. The initial Hg concentrations were based on estimates of 90 species and 180 reactions, Swedish sunlight variations, emissions from earth's surface and several other estimates.

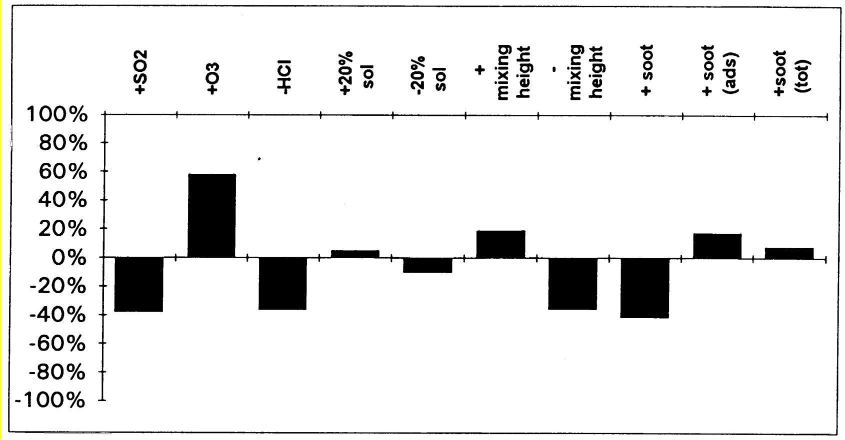

Figure 2: The effect on Hg(II) concentration when changing different parameters. Percentages on the left shows increase or decrease in mercury concentrations, when changing the parameters indicated on the top line[27]*.*

Pleijel and Munthe concludes that the most critical parameters must be SO_2, O_3, Cl^- and pH, and that an effort should be made to estimate these as correctly as possible.

Hg° in air is not very water-soluble and an oxidation must take place to make the mercury deposit with precipitation. The oxidation of Hg° by O_3 is rapid in aqueous solutions. This suggests a much shorter residence time than the well-accepted one year. When this is not observed it might imply that a reaction reducing the Hg(II) back to elemental mercury is counter balancing the oxidation, or that a competing reaction is consuming the O_3. An investigation made by Munthe in 1991[29]proposes the oxidation of S(IV) to be this competing reaction. In the process of oxidising S(IV), three different reactions occur:

1. $SO_2 \bullet H_2O + O_3 \rightarrow SO_4^{2-} + 2H^+ + O_2$
2. $HSO_3^- + O_3 \rightarrow SO_4^{2-} + H^+ + O_2$
3. $SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2$

The oxidation of Hg° in aqueous media is thought to be:

1. $Hg° + O_3 + H_2O \rightarrow Hg^{2+} + 2OH^- + O_2$

Experiments demonstrated that in acidic solutions, Hg° was consumed much more rapidly than S(IV), while in neutral and alkaline solutions S(IV) was consumed to a greater extent than Hg°. S(IV) can also reduce Hg^{2+} to Hg° in aqueous solutions. From the information above a high concentration of oxidised mercury species in areas with low SO_2 concentration (open oceans) should be expected, this is, however not observed and it might imply that the model is too simple.

In 1995 Hall[5] performed a study on the gas phase reaction of Hg°with O_3. The importance of this reaction in the global cycling of mercury has been an issue in scientific circles for some time. In the gaseous phase Hg° can be oxidised by O_3 into both a gaseous and a solid product:

1. $Hg^{\circ}_{(g)} + O_{3(g)} \Rightarrow HgO_{(g)} + O_{2(g)}$
2. $Hg^{\circ}_{(g)} + O_{3(g)} \Rightarrow HgO_{(s)} + O_{2(g)}$

Hall tested the influence on the rate of the reactions of changing different parameters. Among others, he tested the influence of sunlight that apparently increased the reaction rate. Changing the relative humidity gave no effect. His conclusion was that albeit the slow rate of the reaction, it was important for the transport and transformation of atmospheric Hg.

A study of the fate of mercury species after oxidation by ozone[30] demonstrated the significance of the presence of HCl. In the absence of HCl, Hg(II) was reduced back to Hg° as a result of the formation of sulphite complexes $HgSO_3$ and $Hg(SO_3)_2^{2-}$, and their subsequent transformation to Hg°. When HCl was present, $HgCl_2$ complexes would be formed. Hg(II) was then not available for reduction by dissolved SO_2 since the $HgCl_2$ was preferentially formed, and scavenged from the atmosphere by wet deposition. $HgCl_2$ is thought to be the major component of the gaseous divalent mercury (GDM) fraction.

Analysis performed in areas substantially polluted by mercury[4], have revealed that a significant fraction of the total mercury concentration is present in the aqueous phase. There is evidence that Hg is adsorbed onto soot particles, and as a result the total Hg concentration in water droplets exceeds the steady state value for Hg(II).

Mercury is removed from the atmosphere by both wet and dry processes acting on Hg°, $Hg(II)_{(g)}$ and $Hg(II)_{(p)}$. Which is the dominant process, depends on the individual concentrations of the different mercury species. If there are high concentrations (>100 pg/m^3) of $Hg(II)_{(g)}$ and $Hg(II)_{(p)}$ they will control the overall deposition, both wet and dry. Moderate to low concentrations of $Hg(II)_{(g)}$ and $Hg(II)_{(p)}$ will make the wet deposition dependent on the oxidation of Hg° in gaseous and aqueous phase by ozone or other oxidants.

Soil is considered a net sink for the Hg pool present in the atmosphere. The Hg is introduced to the soil mainly by wet deposition through rain. In forested areas the dry deposition is of equal or greater importance than wet deposition[2]. Three different processes can deposit Hg:

- Adsorption and oxidation of gaseous Hg°[31].
- Uptake of Hg° by stomata[32].
- Adsorption of gaseous Hg(II) and particulate Hg.

The dry deposited Hg is thought to be washed off the plant surfaces and thereby elevating the Hg concentrations in through-fall over those in precipitation. The exchange of Hg between air and vegetation, besides forested areas, has not been well described and few data exists. The potential importance of these processes is only now being recognised.

Regarding the air-water exchange, flux-measurements indicate that there is no net transfer in either direction. The large majority of aquatic ecosystems studied so far has been found to contain dissolved gaseous mercury (thought to be mostly Hg°), at concentrations which are supersaturated relative to the equilibrium values predicted by Henry's law[2].

The re-emission of Hg from terrestrial surfaces is very important in the cycling of atmospheric mercury[33]. Experiments give evidence for volatilisation of Hg from a large variety of vascular plants, non-vascular plants (lichens and mosses), algae, the oceanic surface, mercuriferous and non-mercuriferous soils and Hg-containing solid waste deposits. Quantifying the magnitude and direction of fluxes in air-water and air-soil exchange processes involving Hg, will be an important challenge in the mapping of the mercury cycle.

1.5.2.2 Modelling the cycle of atmospheric mercury

The environmental cycling of mercury is extremely complicated, and involves a multitude of chemical and physical processes that affect its toxicity and mobility. As the knowledge of mercury and all its properties increases, the models will become more complex allowing much more detailed descriptions of the transport and transformations occurring in the atmosphere[27].

Incomplete understanding of emissions, transformations and deposition processes has hindered the numerical modelling of mercury. A model from 1994[22] is visualised in Figure 3. The model deals with a wide spectrum of fluxes, but has very little description of the chemical and physical forms in the atmosphere.

The early modelling gave limited information, and was not sufficient for obtaining a confident chemical discrimination of gaseous mercury concentrations in ambient air. Still it returned valuable information on what kind of data that was necessary to improve the models. Regarding both flux measurements and speciation, promising new methods are now being developed in order to collect the desired information[17].

The atmospheric cycling of mercury is only a part of the complete mercury cycle. In the future the increased amount of available data might make it possible to also include water and terrestrial media in a larger multimedia model[17].

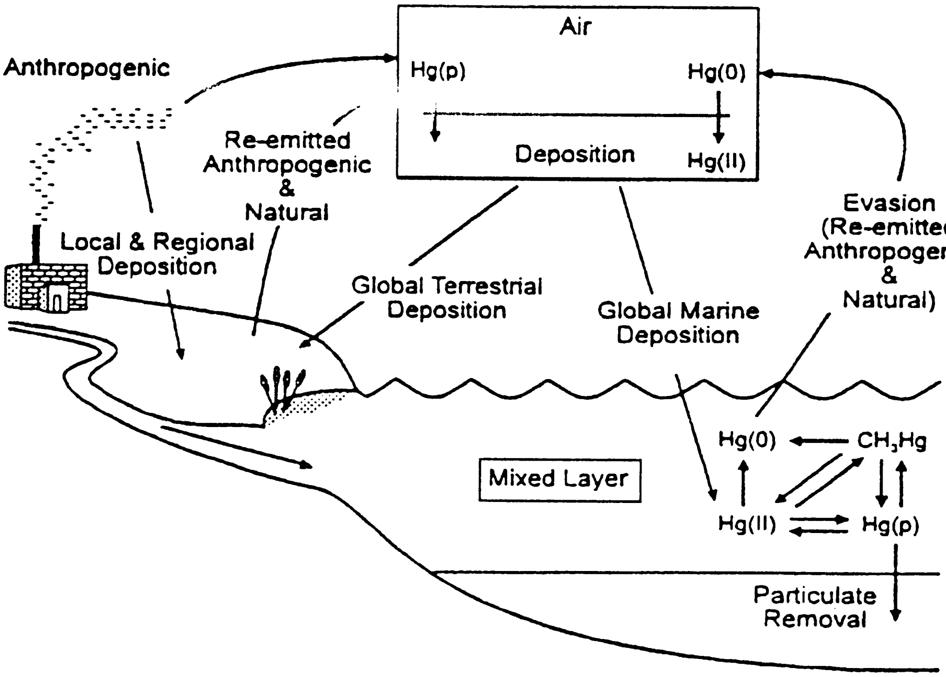

Figure 3: Global mercury cycle model[22].

1.6 Speciation

Many problems and challenges are connected with the aspects of speciation. How can the different species be separated from each other? Is it necessary to separate the species in the line of sampling, can the species be separated during analysis, or is an additional separation step required? Another problem is the mostly very low amounts existing of each species. In most cases a form of concentration step is essential to be able to detect and quantify the species. Dealing with such low concentrations, contamination might also be a challenge. Samples can be contaminated via ambient air, by equipment used for sampling and analysis, and also by the operator. In the case of species sampled from air the location of the sampling can be crucial. Even small amounts of the species of interest evaporated from walls, the ground or other surroundings, might alter the measured result significantly. These, and a multitude of other considerations, must always be an issue working with speciation and trace analysis.

1.6.1 Speciation of atmospheric mercury, what has been done?

Reactive gaseous mercury (RGM) has been defined by Brosset[34]. He states that Hg-compounds (Total Hg), can be divided into two groups (see table 1). The first group is named Hg^{I} and represents the Hg-compounds insoluble in water. These compounds have high Henry Law constants. The Hg^{I}-group is further divided into Hg^{Ia} and Hg^{Ib} representing elemental vapour mercury (Hg°) and mercury bound to two organic groups ($(CH_3)_2Hg$), respectively. In atmospheric studies the main interest has been in the water-soluble species in group Hg^{II}. Brosset has divided this group further into two subgroups. Hg^{IIa} species will be reduced to Hg° both by $NaBH_4$ and by $SnCl_2$. This is the specie reactive gaseous mercury (RGM), and it is believed to represent inorganic Hg. Hg^{IIb} are compounds that will be reduced to Hg° by $NaBH_4$ but not by $SnCl_2$.

Table 1: Brosset's classification of mercury species[34]. H is the non-dimensional Henry law constant.

Total Hg (Hg_T)			
Hg^I (H ~ 0.3) Insoluble in water		Hg^{II} (H ~ 10^{-4} or lower) Water soluble	
Hg^{Ia}	Hg^{Ib}	Hg^{IIa} (RGM) Reduced by $NaBH_4$ and $SnCl_2$	Hg^{IIb} Reduced by $NaBH_4$, not by $SnCl_2$
Metallic vapour Hg°	Org-Hg-Org e.g., $Hg(CH_3)_2$	Inorg-Hg-Inorg e.g., Cl-Hg-Cl	Org-Hg-Inorg e.g., CH_3HgCl

RGM has been collected on various media, and was also thought to be the species collected on the kind of denuders tested out in this work. In 1997 Xiao et al.[35] demonstrated that these denuders also collected the Hg^{IIb} compounds from Brosset's definition[34]. The collected fraction then contains both the inorganic divalent species and the methylated CH_3HgCl species, the latter not being a part of the defined reactive group. The term RGM is still commonly used to describe this fraction, but a more correct designation is gaseous divalent mercury; GDM, which will be used in this paper. GDM will consequently be used to describe water-soluble Hg compounds that will be reduced by $NaBH_4$ and/or $SnCl_2$, to Hg°. The term RGM will be applied only when appropriate.

The term “Total Gaseous Mercury” or “TGM” covers, as the name implies, all gaseous forms of mercury (all forms in table 1). The term is however also used for the mercury sampled on gold traps (see Total gaseous mercury (TGM)). Most of the TGM consists of elemental mercury, Hg°, which proved to be quantitatively collected onto gold traps. On the other hand, the other gaseous species seem to be collected to varying (and unknown) degrees. Using the term TGM for the fraction of mercury collected by, for instance, the Tekran monitor (see Total gaseous mercury (TGM)), might therefore be misleading. Although the name TGM may possibly be incorrect, it is still the commonly used phrase for the sampling fraction, and will therefore be applied throughout this study.

“Total Particulate Mercury” or “TPM” will in the following be defined as all atmospheric mercury associated with particulate matter.

The process of amalgamation of mercury on gold and silver is important not only for the sampling of TGM, but also as a concentrating step in the analysis of other mercury species. Amalgams are alloys between mercury and a noble metal. Most sampling and concentrating traps employed in the quantification of mercury species are filled with either glass beads or silica sand coated with thin gold films. A study from 1999[36], concluded that adsorption of mercury onto thin films of gold or silver is a complicated multi-atomic process involving a weakly bound adsorption state. It was also concluded that the saturation level on these thin films depended both on adsorption temperature and the concentration of mercury in the gas flow over the surface. Problems with over-saturation are not very common dealing with the low mercury concentrations in ambient air.

Practically all analysis on atmospheric mercury species today are carried out with atomic absorption spectroscopy (AAS) or atomic fluorescence spectroscopy (AFS). The AAS instruments are quite simple, commonly available and fairly inexpensive. They are usually smaller (and simpler) than the AFS instruments, and therefore more mobile. The AFS instruments are more sensitive, but also more complex and expensive. Mercury has a high vapour pressure, and can thus be analysed without the use of an atomising flame. The techniques are then named cold vapour (CV) AAS or AFS.

Manual methods imply that the sampling process and the analysis are separated, and both have to be initiated with aid from an operator. Sample preparations between sampling and analysis can also be included.

The automatic methods utilise online systems/monitors. After the system is started, the whole process is automatic, and no support from the operator is required. After initial preparations, the monitor can perform sampling, preparations and analysis before the measured result is displayed. When a cycle is finished, another one will start automatically.

1.6.1.1 Total gaseous mercury (TGM)

Normally Hg° constitutes at least 90% of mercury in ambient air and is therefore, by a large amount, the main component in TGM. Mercury can be adsorbed onto a number of materials, and many of these have been tested out for sampling of Hg in ambient air over the last decades. Examples of such materials are activated carbon (plain or treated), magnesium oxide or magnesium copper oxide, lead sulphide and several different liquid impingers. Another method of collecting mercury is to take advantage of its ability to amalgamate with noble metals like gold and silver. Today this principle is almost exclusively the one used in sampling of TGM[20].

The most common precious metal trap is today covered with gold, but some also have silver. All the manual methods are very similar and some of them have been used for twenty years without major changes. The material in the trap can be solid metal gauges or wool, or it can be glass beads or silica sand coated with gold or silver. The amalgamation material is kept inside an about 10 cm long quarts tube. In general the TGM is collected by pulling air through the trap. During analysis the trap is heated to temperatures between 400°C and 700°C . The mercury is then released and transferred directly to the detector, or more commonly via an analytical pre-concentration trap usually similar to the sampling-trap. The mercury is then thermally desorbed again and transported to the detector. At least two automated TGM samplers are commercially available today. The Mercury Analyser Model GARDIS-1A (based on an AAS principle), produced at Ecological Spectroscopy Lab., Institute of Physics, Vilnius, Lithuania, and Tekran Model 2537A-Mercury Vapour Analyser (based on an AFS principle) produced by Tekran Inc., Toronto, Canada[37].

1.6.1.2 Total particulate mercury (TPM)

Conventionally TPM has been collected using particulate filters of different designs. Most commonly the filters are made of PTFE (polytetrafluoroethylene), or quartz fibres. The filters are brought to the laboratory and leached/digested by acid. The mercury is reduced to Hg° using $SnCl_2$ and collected on gold traps by flowing argon through the solution and trap. The trap is then thermally desorbed and analysed by CVAFS or CVAAS[37].

The disadvantages of the conventional method are several filter/sample-handling steps that easily can cause contamination. A sample preparation can take hours and maybe even days. The very small amounts of TPM in the air and the lack of very sensitive analysis has also made it necessary to have as large a surface area as possible, and very long sampling periods. Today the availability of much more sensitive analysing methods entails that less sample material is required. It is possible to have smaller sample surfaces, shorter sampling times and a lower flow rate. In 1998[38], a new device for sampling and determination of TPM was tested. This device consists of a quartz trap (made of two quartz tubes) containing the quartz fibre filter, 6 mm in diameter, weight 80 g/m^2 and a penetration DOP% (0.3μm) < 0.002. The trap can be placed directly into an oven/pyrolyser where the mercury is desorbed for analysis. Using this trap implies minimal handling of the samples, no sample preparation, and the analysing time is maybe as short as 10 minutes. The tests results were in good agreement with conventional methods. The automated Tekran Model 1135 Particulate Mercury Unit made by Tekran Inc., Toronto, Canada is based on the particulate trap principle and is commercially available today.

1.6.1.3 Reactive gaseous mercury (RGM) and gaseous divalent mercury (GDM)

The importance of these species have been recognised for the last two decades but limited investigations have been made. There has been a lack of suitable sampling methods, mainly because of the extremely low concentrations in ambient air. From 1981 to 1983 Brosset et al.[34] performed a series of experiments on different sampling approaches. At first Hg(II) was collected by pulling air through a column containing the polymer Porapack-Q. The column collected quantitatively Hg^{II}, while it was inert to Hg°. Hg was then thermally desorbed in a N_2-stream at 200°C and transferred to an Au-trap for further analysis. The method came out very time consuming because of the slow release of trapped Hg from the Porapack columns, and was abandoned in December 1983. Collection of Hg(II) by bubbling air through water solutions was also tested out. It was discovered that the Hg(II) in such solutions may (to a substantial degree), be decomposed by daylight. Variations in the degree of decomposition were observed, and were thought to be caused by dissimilar stabilities of the different Hg(II) complexes. The water in the bubbler was then exchanged for NaCl in order to get the strong complex $HgCl_4^{2-}$. An oxidation of Hg° was then revealed leading to a positive bias in the measurements. When the pH was increased it led to a reduction of Hg(II) giving a negative bias.

According to Xiao et al.[35] there were reports in 1996 of promising results from experiments using cation exchange membranes for sampling of GDM. However there has apparently not been any published information on the subject afterwards.

In 1995 Stratton and Lindberg[39] released the first reports on the use of a high-flow refluxing mist chamber in the sampling of RGM. The refluxing mist chamber (MC), was developed in 1985 at the NASA Langley Research Centre. It was used for various studies of trace gases in the atmosphere including formaldehyde, carboxylic acids, HCl and Cl_2. The design of the MC can be viewed in Figure 4.

The volume of the chamber and the refluxing top was 75 ml and minimum amount of solution inside was 8 ml. 15-20 ml of a 0.5% HCl fresh solution was filled into the chamber. The nebulizer produced a fine mist of the absorbing solution, and water-soluble species were extracted from the air stream. Though not visible in figure 4, the nebulizer (by the air inlet) had four nozzles. The ambient air was pulled through the chamber by a pump at a flow rate of about 15-20 l/min. If it was necessary, more absorbing solution was added during sampling. After sampling, $SnCl_2$ was added to the solution to reduce the RGM to Hg° (which was collected on a gold trap by purging the solution with Ar). Several tests were performed in an attempt to validate the method. The tests indicated that there were no Hg° collected in the solution, no co-sampled TPM, no significant oxidation of Hg° to Hg(II) by O_3 and no photochemical effects.

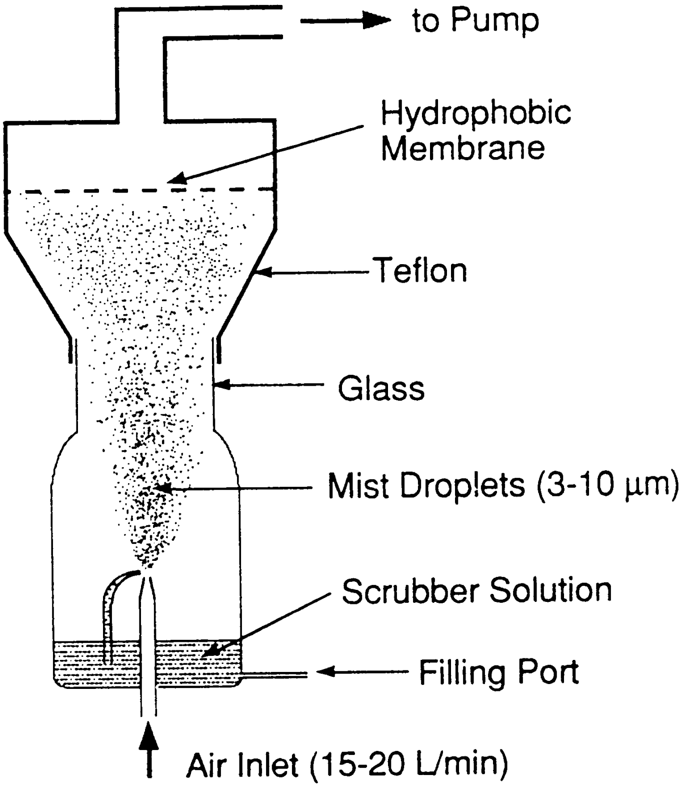

Figure 4: The design of a refluxing mist chamber in 1995[39].

In 2001 the group published another paper on the use of MC as a device for sampling RGM[40]. Only small adjustments have been made to the method from 1995. The MC has a single nozzle instead of four, 30 ml absorption solution is used instead of 20 ml and a soda lime trap is added in the sampling line to protect the mass flow meters from acid vapours. See design in Figure 5. After further testing the group concluded that the MC gave a reasonable result under typical conditions but that a significant breakthrough was observed at very high Hg concentrations.

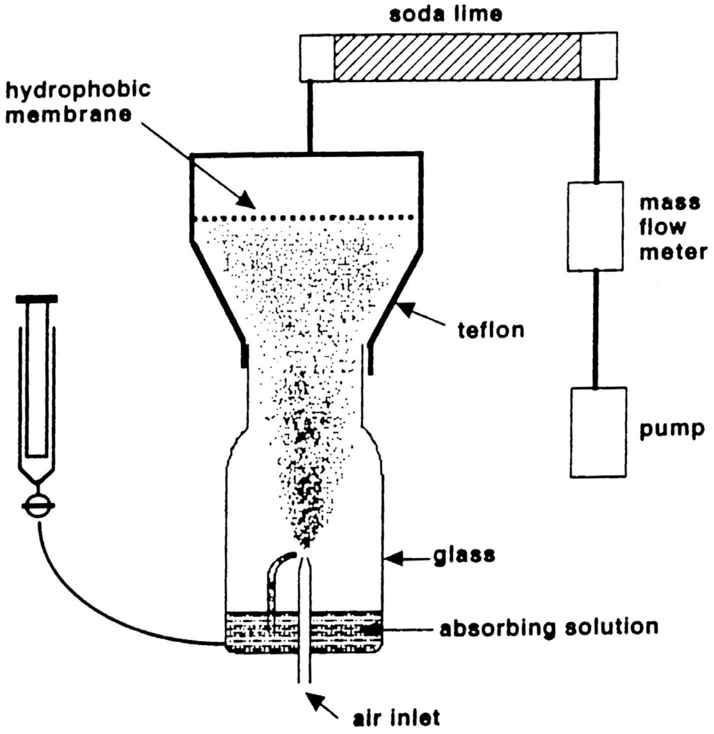

Figure 5: The design of a refluxing mist chamber in 2001[40]. On the left , the single nozzle is illustrated.

Denuder techniques have been used in measurements of gas phase species in the atmosphere for decades. Among the collected species are ammonia, sulphur dioxide, nitric acid, nitrogen dioxide and chlorinated organic compounds. Denuders are tubes of various sizes and materials. They are coated on the inside with diverse materials depending on the compound they are supposed to collect. The "target" compound is scrubbed from the air by pulling it through the denuder. The air passes through while the compound sticks to the coating. Gold or silver coated denuders have been applied for measurements of TGM in air. In 1997 Xiao et al.[35] reported the first experiments using a KCl coated denuder in sampling of gaseous divalent mercury species in air. The denuders consisted of 55 cm long glass tubes with an i.d. of 6 mm. The inner walls were coated using a saturated KCl in methanol solution at a temperature of 50°C. The coating was inspected under an electron-microscope and the walls appeared well coated, covered evenly by tiny crystals of KCl. Sampling was done by pulling air (using a pump), through the denuder for 24 hours at a flow rate of 1 l/min. The sample was then extracted in HCl , reduced by $SnCl_2$ and analysed by CVAFS. The reduction step with $SnCl_2$ implied that only RGM would be analysed albeit the denuder was proved to collect CH_3HgCl as well. After several tests the group concluded that KCl denuders could quantitatively collect Hg(II) from air retaining no Hg°. The efficiency seemed to be good (about 98%), and sampling and analysis relatively easy. Compared to the mist chamber method the denuders had the advantage of low possibility of sampling artefacts of Hg(II) formation through Hg° oxidation or dissolution of co-sampled TPM. This is due to the denuder principle of gaseous-molecule-only. They also concluded that the KCl denuder could be useful for sampling CH_3HgCl if an adequate elution solution is applied.

The same group published an article in 1999[3] reporting on several modifications made to the denuder system from 1997. Annular denuders had been tested out. They consisted of two quarts tubes inside each other with about 1 mm spacing and sandblasted annulus walls. The new denuders had an effective coating length of 20 cm compared to the old tubular denuders having an effective length of 50 cm. The effective area was still larger on the annular denuder. The coating was the same. Thermal desorption had been tested out, meaning that the whole GDM fraction was introduced into the analyser. The denuders were also cleaned by heating them. Samples were taken by pulling air through the denuder at a flow rate of 6-9 l/min allowing much larger volumes of air than previously. The denuders were heated to 40-50°C to prevent KCl from dissolving in condensation. The Hg(II) was released from the denuder by desorbing at 450°C for about 10 min. The sample was pyrolysed before pre-concentration on gold traps in the analyser, using quarts beads in a quarts column at 900°C. An automated sampling and analysis line was also tried out. Testing showed smaller and less variable blanks and lower detection limits (<1 pg/m^3) in addition to the sample preparation being eliminated. Besides these investigations by Xiao et al., there have been parallel studies performed by scientific groups in Canada and USA.

Recently Tekran Inc., Toronto, Canada, presented an automated KCl annular denuder system.

1.6.2 Areas of special interest

In some areas there has been taken a special interest in mapping the distribution of mercury species in the ambient air. The possible enhanced concentrations of the more reactive species in these areas may cause severe damages to the environment. Examples are heavy industrialised districts and the Arctic region.

1.6.2.1 Industrial sources, flue gases

The physical and chemical processes between mercury and other flue gas components are poorly known. The chemical system of a flue gas is very complicated and contains a wide variety of components. Typical constituents in a combustion flue gas are O_2, HCl, Cl_2, SO_2, NO_2, N_2O, NO, NH_3 and H_2S. Until recently only the total mercury concentration was measured in flue gases. The last decades several attempts have been made on modelling the chemistry of Hg and its species in flue gases[41]. The equilibrium modelling predictions seems to give a reasonable approximation of the proportions of different Hg-forms, but the quality of a model depends highly on number of Hg species considered, quality of corresponding thermo-chemical data, and the total chemical composition of the system. Experiments under laboratory conditions suggest the following reactions to occur in the flue gases.

Oxidations:

1 $2Hg^{\circ}_{(g)} + O_{2(g)} \Rightarrow 2HgO_{(s,g)}$
2 $Hg^{\circ}_{(g)} + Cl_{2(g)} \Rightarrow HgCl_{2(s,g)}$
3 $2Hg^{\circ}_{(g)} + Cl_{2(g)} \Rightarrow Hg_2Cl_{2(s)}$
4 $Hg^{\circ}_{(g)} + 2HCl_{(g)} \Rightarrow HgCl_{2(s,g)} + H_{2(g)}$
5 $2Hg^{\circ}_{(g)} + 4HCl_{(g)} + O_{2(g)} \Rightarrow 2HgCl_{2(s,g)} + 2H_2O_{(g)}$
6 $4Hg^{\circ}_{(g)} + 4HCl_{(g)} + O_{2(g)} \Rightarrow 2Hg_2Cl_{2(s)} + 2H_2O_{(g)}$
7 $Hg^{\circ}_{(g)} + NO_{2(g)} \Rightarrow HgO_{(s,g)} + NO_{(g)}$

Reductions:

1 $HgO_{(s,g)} + SO_{2(g)} \Rightarrow Hg^\circ_{(g)} + SO_{3(g)}$

2 $3HgCl_{2(g)} + 2Fe_{(s)} \Rightarrow 3Hg^\circ_{(g)} + 2FeCl_{3(s)}$

3 $HgO_{(s)} + CO_{(g)} \Rightarrow Hg^\circ_{(g)} + CO_{2(g)}$

Hg° is the dominant specie in the reducing conditions of gasification flue gases. The decreasing temperatures of a combustion flue gas induce the formation of Hg(II). Current analysis indicates that >50% Hg° reacts to form Hg(II) in coal combustion gases. As the flue gases cool down, it is important to consider the significant fraction of vaporised Hg that adsorbs on residual carbon particles. The speciation procedures must then involve both gaseous and solid phases. Combinations of modelling and measurements indicates that chlorine enhances vaporisation of Hg and inhibits nucleation and condensation at temperatures between 100-270°C[41]. At temperatures below 450°C $HgCl_{2(g)}$ is the dominant species. As the temperature rises $HgCl_{2(g)}$ reacts with H_2O to produce $HgO_{(g)}$, that in turn decomposes to Hg° and O_2. Consequently high temperatures will favour the Hg° form.

Regarding speciation in flue gases there has been significant progress in investigations, but no validated method is still available. There is a lack of published results for speciation measurements in gasification systems. Reliable measurements will require more development and validation. Speciation in flue gases is important in minimizing emissions and understanding their atmospheric fate and transportation[41]. The formation of Hg(II) species can lead to far more deposition on a local and regional scale. Nevertheless, in case of the flue gases this formation is generally considered an advantage. The Hg(II) forms are much more water-soluble and are thus easier to capture by wet scrubber pollution control. Hg° on the other hand is fairly unreactive and is much more likely to enter the global atmospheric cycle. To describe and quantify the different Hg species in the gas is then crucial in the development of suitable scrubbers. A potential problem might lie in the fact that some scrubbers seem to initiate Hg° formation and even more Hg° is released then without the scrubber function.

1.6.2.2 The Arctic environment

The discovery of depletion of surface ozone at Alert in the Canadian Arctic in spring was first reported by Bottenheim in 1986, and Barrie in 1988[42]. The concentration of ozone dropped close to zero in frequent episodes in a two - three months long period following the polar sunrise. The episodes were accompanied by elevated bromide concentrations and gaseous Br is thought to cause the loss of ozone[43], when the following reaction takes place.

$$Br + O_3 \Rightarrow BrO + O_2$$

Large amounts of Br is produced in spring by photolysis of bromoform (CH_3Br) emitted from algae in the Arctic Ocean[44]. Measurements of light hydrocarbons have indicated that photo-chemically induced chlorine reactions also takes place[45].

Recent installations (1995-2000), of automatic monitoring devices for TGM at Arctic research stations in Alaska, North Greenland and in the Canadian and Norwegian Arctic, have made it possible to watch changes in TGM concentrations very closely. Observations have been made that TGM undergoes depletion episodes closely following ozone[6].

Schroeder et al.[6] suggests that the springtime conversion of Hg° results from an undefined chemical oxidation mechanism, and that one or more species with shorter atmospheric residence time is formed (e.g. Hg(II)).

Measurements made by Boudries and Bottenheim in 2000[46] reveals that even when the mixing ratio of O_3 is very low, probably because of the reaction:

$$Br + O_3 \Rightarrow BrO + O_2$$

the equilibrium between Br and BrO is shifted towards Br. It is suggested that this is due to the reaction of Hg° with BrO:

$$Hg^\circ + BrO \Rightarrow HgO + Br$$

The conclusion will then be, that the formation of oxidised Hg species results mainly from reactions with BrO and not Br.

1.7 Goals

The object of the following study will be to develop a rugged method for sampling and quantifying GDM. The method should be specific and precise as well as able to collect and quantify very low amounts of GDM (pg/m^3).

In order to be able to measure the GDM concentrations in the mentioned target areas, the method will also have to be suitable for working in the field. E.g. a simple, small and portable system.

Working with limited budgets, the instrument parts should be as inexpensive as possible. Procedures should not be time consuming, especially those involving an operator.

After development and validations, the method ought to be tested out in target areas.

2 Preliminary considerations and choices

No GDM sampling or analytical system was available at Norwegian Institute for Air Research (NILU), prior to this study. All solutions had to be worked out and chosen. The first approach to the GDM problem was therefore a stay for purposes of study in Gothenburg, Sweden. The use of the two most promising sampling methods, and to some degree the analysis, was established. The use of mist chambers were demonstrated by Ingvar Wangberg and Elsmari Lord at Swedish Environmental Research Institute (IVL Svenska miljøinstitutet AB)[47]. The demonstrations of denuders were performed by Xinbin Feng, Katarina Gårdfelt and Jonas Sommar at Chalmers university of Technology[48].

2.1 Sampling method

After considering both methods, advantages and disadvantages, the denuder method was chosen to be the most suitable for this study. As the Arctic environment was an area of special interest, the method of choice should be as problem-free as possible to operate there. The use of a liquid in the mist chamber was thought to be a potential problem because of the possibility of freezing in the very low temperatures in the Arctic. The denuders were also thought to be easier to transport, as they were more compact and did not break as easily as the mist chambers.

The annular denuders were preferred, because the large active area on the annular made it possible to increase the sampling flow substantially compared to the tubular. A much higher time resolution could then be obtained (larger volume, more GDM in a shorter time), an advantage when mapping variations in day and night concentrations, and not the least to describe the depletion episodes in the Arctic.

KCl salt, the coating of the denuders, had to be dissolved in a solvent in order to bring it on to the denuder walls. Usually the solvent consisted of water and/or methanol. Methanol had the advantage of being very easily vaporised and a newly coated denuder would be dry and ready after a few hours. Water on the other hand could solve more KCl before saturation. The crystallisation is significantly slower than with methanol, making smaller crystals and a higher degree of coverage on the walls. The scientists at Chalmers university of Technology[48], recommended the use of methanol because of the time saved in the coating process, and methanol was consequently used in this study. Collecting the very small amounts of GDM expected in the following trace analysis would not require a very high capacity on the denuders.

2.2 Sample preparation/introduction

The GDM samples trapped on the denuder walls could be released for analysis either by acid leaking or by thermal desorption. The thermal desorption method would be much less time consuming than the leaking method. Besides saving time and thereby expenses, the absence of sample handling would reduce the sources of contamination considerably. Contamination from sample treatment can be a crucial factor dealing with trace analysis, as was the case here. By thermally desorbing the sample, the KCl coating could also be reused several times to collect new samples after analysis, as is not the case if the sample is extracted and chemically reduced. A new coating procedure would then have been necessary prior to every sampling process. As a result of the considerations, the thermal desorption was the method of choice in this study.

2.3 The introduction system

As thermal desorption was chosen to be the introduction method of the sample, a heating system/oven was required. The Swedish research groups had very simple systems, consisting of only heating wires and power connectors. The heating wires were hanging on tripods, and then open to the air. The advantages of that kind of systems are the ease of changing, fixing and modifying them. On the other hand they are not very stable or easy to control, and the "open heat" can be a hazard to the operator. For this study the "safe" version was preferred, and the oven was built into a closed system.

2.4 The analytical method

Choosing the combination of denuders and thermal desorption, the samples would have to be analysed immediately after sampling. Experiments had shown that the sample was destructed, possibly because of the presence of organic compounds on the denuder coating, shortly after sampling[48]. As a result of this, the whole analytical system would have to be brought out close to the sampling spot whenever the denuders were used. As mentioned in the introduction, virtually all mercury analysis are performed on either AFS-systems, or AAS-systems. The AFS being the most sensitive system, and the AAS being the less complicated and cheaper alternative. Both an AFS-system and an AAS-system were available at NILU. The AFS was too large and complex to move around from field to field, so the small and lighter AAS was selected.

2.5 Specificity of the method

The denuders separate gases from particles based on the fact that gases diffuse much faster than particles. When ambient air is pulled through the denuders, only the gaseous compounds will have "time" to be adsorbed, and the surface will act as a sink for the specific gas of interest.

For a specie/compound to be co-detected together with mercury, giving a positive bias, it would have to be collected both on the denuders and gold traps before absorbing UV light in the same area as Hg. The probability of many species/ compounds following this pattern is not considerable. The "worst case scenario" was thought to be if elemental mercury to some degree was collected onto the KCl denuders. However, Xiao et al.[35] performed series of tests showing that Hg° passed through the denuders without being adsorbed at all.

Several organic compounds might be collected on the denuder surface. Many of them can also absorb UV radiation over large areas and might be a problem, although most organic compounds will combust during the thermal desorption of the denuder samples.

2.6 Field studies

The mentioned depletion episodes in the arctic ordinarily take place in April and May only. To measure if there was any elevated GDM levels during this period, the fieldwork would start only a couple of months after the first introduction to the problem. During these two months, the whole system had to be built and tested out. It was clear that if the field study was to take place, few or no tests or validations could be performed in the laboratory beforehand. Because of the great interest taken in the Arctic depletion episodes, the field study was prioritised above the laboratory tests.

3 Instrumental

The sampling system had to be designed, and most of the parts were custom made at NILU. The denuders were made by a local glass blower using sketches from Chalmers University of Technology in Sweden. An AAS mercury analyser was available for quantification of the GDM samples, but the introduction system had to be designed and some of the parts were made in house at NILU. The following chapters describe the major system parts as well as the sampling line and line of analysis.

3.1 The denuder

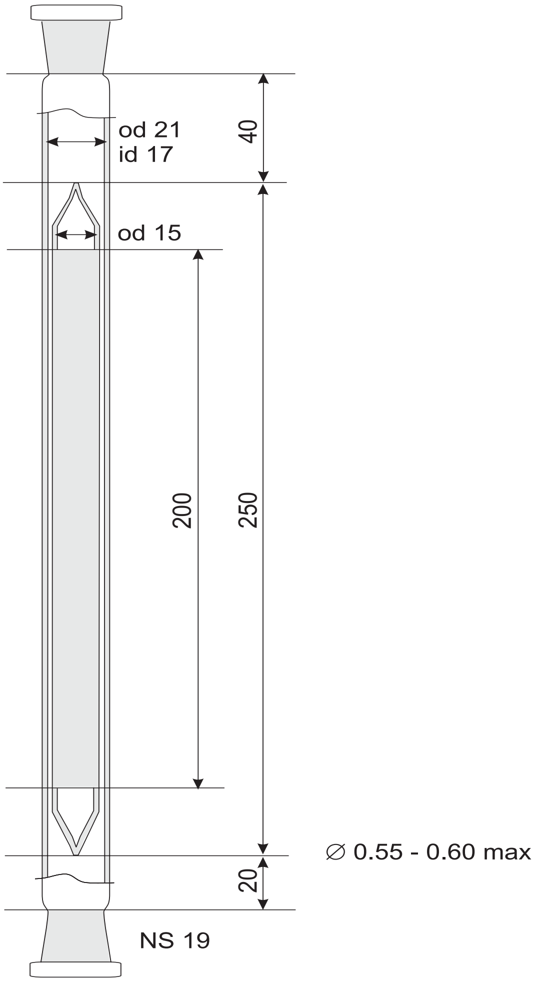

Figure 6: The custom made annular quarts denuder. All measures are given in millimetres.

The denuders used in the following study were custom made by the glassblower company Friedel, in Aurskog, Norway. The design was attained by modifying a sketch of the denuders employed at Chalmers University of Technology in Sweden. Twelve denuders were manufactured. The denuders are of the annular type and each consists of two quarts tubes inside each other. See Figure 6. The outer tube is 370 mm long, has an outer diameter of 21 mm and inner diameter of 17 mm. The inner tube length is 250 mm, and the outer diameter is 15 mm. Top and bottom of the inner tube ends are pointed. The bottom end, pointing towards the inlet of the denuder, is closed. The top end has a small hole to relieve the internal pressure during desorption. An area, about 200 mm long, on the inside of the outer tube and outside of the inner tube, is sand blasted. The rougher surface makes the coating stick better to the denuder walls, and the area is called "the active area".

3.2 Sampling

3.2.1 Sampling box

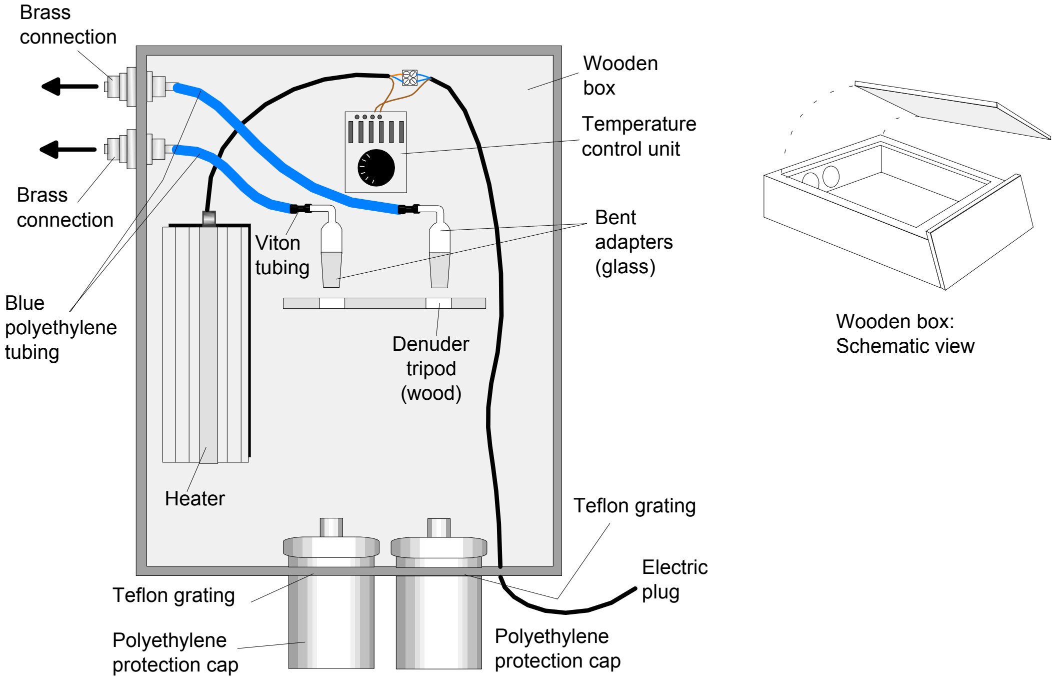

Figure 7: The wooden sampling box. On the right a view of the box from the outside. No denuders are connected.

The wooden sampling box was custom made at the instrument laboratory at NILU. The box is made of veneer plates and is about 60 cm high, 40 cm broad and 10 cm deep. See Figure 7. Polyethylene caps and Teflon gratings protect the air inlets at the bottom of the box. Over the Teflon grating there is a Teflon connection where the denuders are placed during sampling. The denuders are also connected to bent glass adapters, via viton and blue polyethylene tubing, and through brass connections on the sampling box wall. A small heater with temperature control, is placed inside the box. The box is closed using a "lid", also made of veneer.

3.2.2 *Pumps*

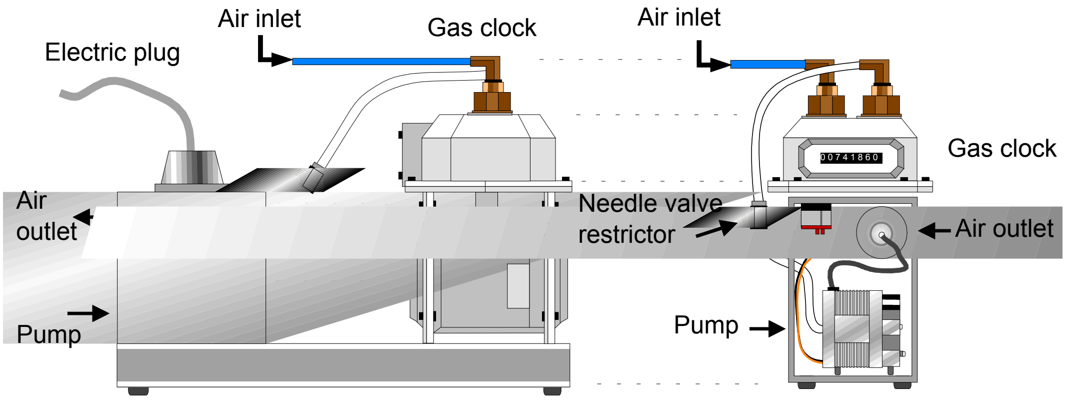

Figure 8: Gas pump used for sampling. On the left a side view, on the right a front view.

The pumps used for sampling were small gas pumps (See Figure 8), type VP-0125. They are vacuum linear piston pumps, with a maximum vacuum of 680 mbar. Maximum airflow is 7 L/min. The flow can be restricted by the use of a small needle valve restrictor (see figure). The frequency of the pump is 50 Hz.

The pump is connected to a REMUS 3 gas clock made by Schlumberger LTD.

3.2.3 *Sampling system*

The system set up is described in Figure 9. Normally the most convenient placing of the sampling box is on the wall of a building, as described in the figure. The pumps are not water resistant, and have to be placed inside. An electricity connection is also necessary to give power to the small heater in the box. Alternative placings of the box is on a pole or a tripod. For sampling purposes, the denuders are put in the box, inlet pointing towards the bottom were a Teflon connection keeps them steady, and connected to the tubing with bent glass adapters. The tubing, that connects the box and the pumps, is pulled through the wall, as is the heaters electricity wire. The small heater shall keep the temperature at about 40°C. Heating is necessary to avoid condensation in the denuders, as the water can dissolve the KCl salt. When the pumps are turned on, air is pulled through the denuders and the system. The plastic shield and Teflon grid at the air inlet protects the denuders from snow and large particles. When the air passes through the KCl coated denuders, the divalent mercury species will be collected on the denuder walls when $HgCl_4^{2-}$ complexes are formed.

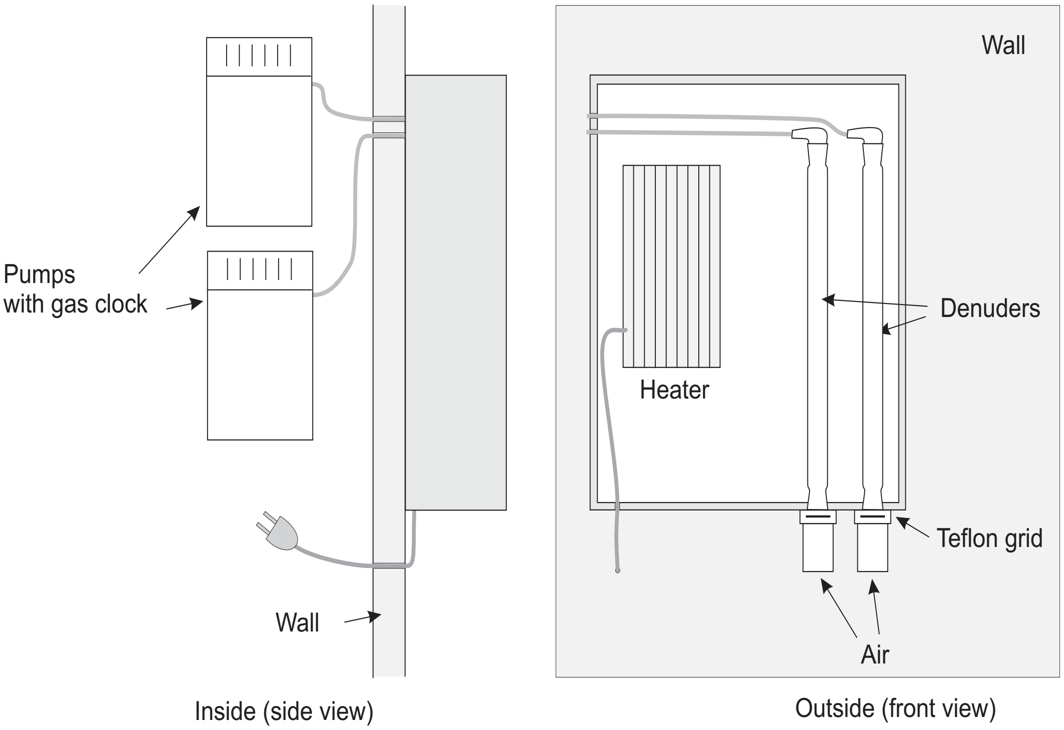

Figure 9: The sampling line. The front view shows the interior of the sampling box. The side view shows how electrical wire and tubing are pulled through the wall.

3.3 Analysis

The analyser has to be turned on at least one hour before any measurements are performed. The lamp in the monitor needs to be heated to give stable results.

3.3.1 Calibration

A gas tight syringe is used to take out known volumes of saturated mercury air from the vessel in Figure 10 below. The unit is made in house at NILU. Metallic mercury is kept in a plugged glass vessel that is placed in a polystyrene box to stabilize the temperature within. The box is carefully shaken from time to time to keep the air fully saturated. A thermometer is placed down in the vessel, and the right temperature is recorded every time a volume of mercury is taken out. The correct amount of mercury, depending on the temperature, can be calculated according to the table in Appendix 3.

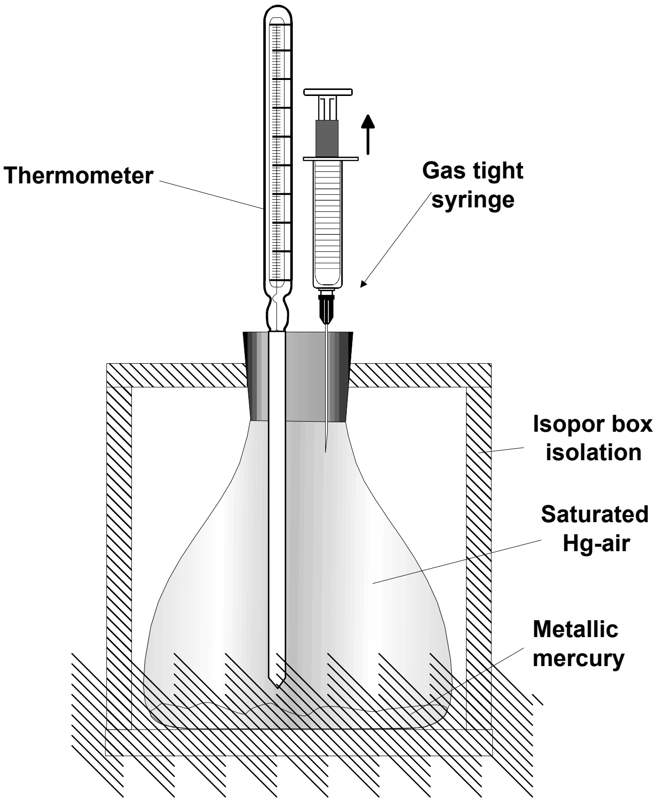

Figure 10: Calibration vessel containing saturated mercury air over metallic mercury.

3.3.2 Mercury AAS analyser

The Mercury Analyser Model GARDIS-1A is an automatically operated mercury monitor, produced at Ecological Spectroscopy Lab., Institute of Physics, Vilnius, Lithuania. Figure 11 is a simplified diagram of the GARDIS' principles of operation. The GARDIS is based on the Atomic Absorption Spectroscopy (AAS) principle. An aerosol filter at the gas inlet protects the system from particles and humidity. The sampling trap and the analytical trap are identical, and consist of gold threads kept in small quarts tubes. Both traps are heated to about 700°C during detection. The optical cells are made of Pyrex glass, internal diameter about 3 mm and length about 150 mm. The optical windows are made of quarts, and are attached to the cell with thermally resistant glass glue.

The light source is a low-pressure EDL (Electrode-less Discharge Lamp) mercury lamp, excitated by an external electromagnetic field of about 50 MHz. The lamp has only one dominating spectral feature in the near UV range, and this is 254 nm (Hg resonance spectral feature).

The chopper alternates the beam of light between the sample cell and the reference cell in order to compare the light intensity between the two. The chopper modulation is about 20 Hz.

A vacuum phototube with maximum sensitivity in the region 220–260 nm performs the light detection. The tube is practically "blind" outside the region 220–330 nm, and the spectral feature 254 nm is therefore virtually the only one to which the phototube responds. the manufacturer states that this is checked by indirect observations, by investigating the light absorption law with respect to the Hg concentration in the optical cell. The Beer–Lamberts law remained valid over a wide range.

The pump frequency is 50 Hz and the "normal" flows are 1 L/min during sample introduction, and 10 ml/min during desorption and analysis. The sample introduction flow was however changed to 200 ml/min to perform all the following experiments.

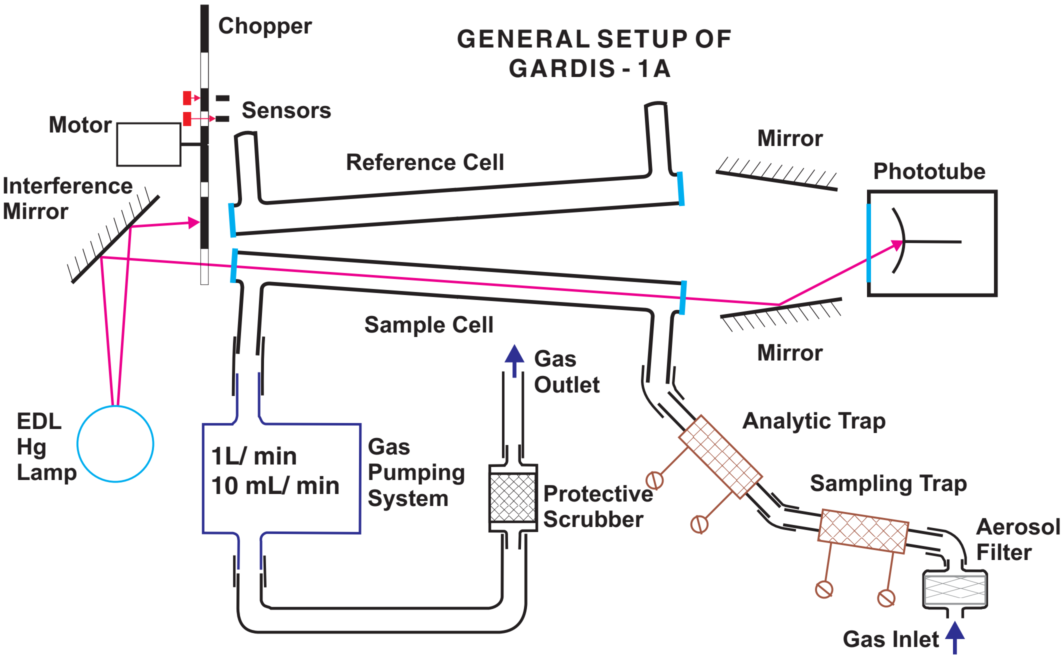

Figure 11: Simplified diagram of the GARDIS operation principle. Explanations are in the text above.

3.3.3 Denuder oven

The oven system was custom made at the instrument laboratory at NILU. It was designed into a standard electrical wall enclosure for ease of access to internal components, transport, and for safety reasons. The heat capacity of the system was unfortunately such that the "door" had to be left open during operations. Figure 13 gives a schematic view of the denuder oven system, while Figure 12 shows the interiors of the oven itself. The figures and the following descriptions regard the initially designed oven. It was later modified as described in section 4.2.7.

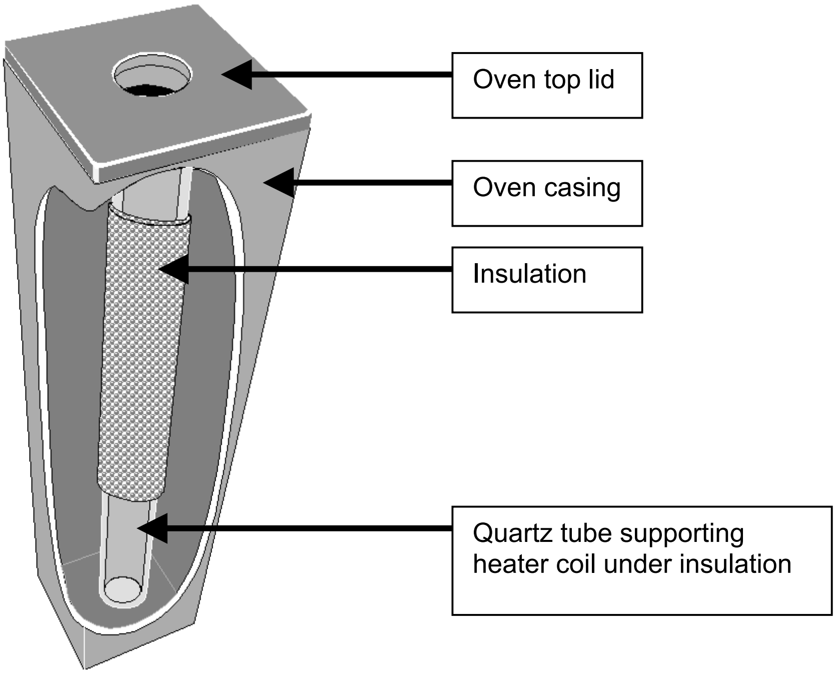

Figure 12: The interior of the denuder oven.

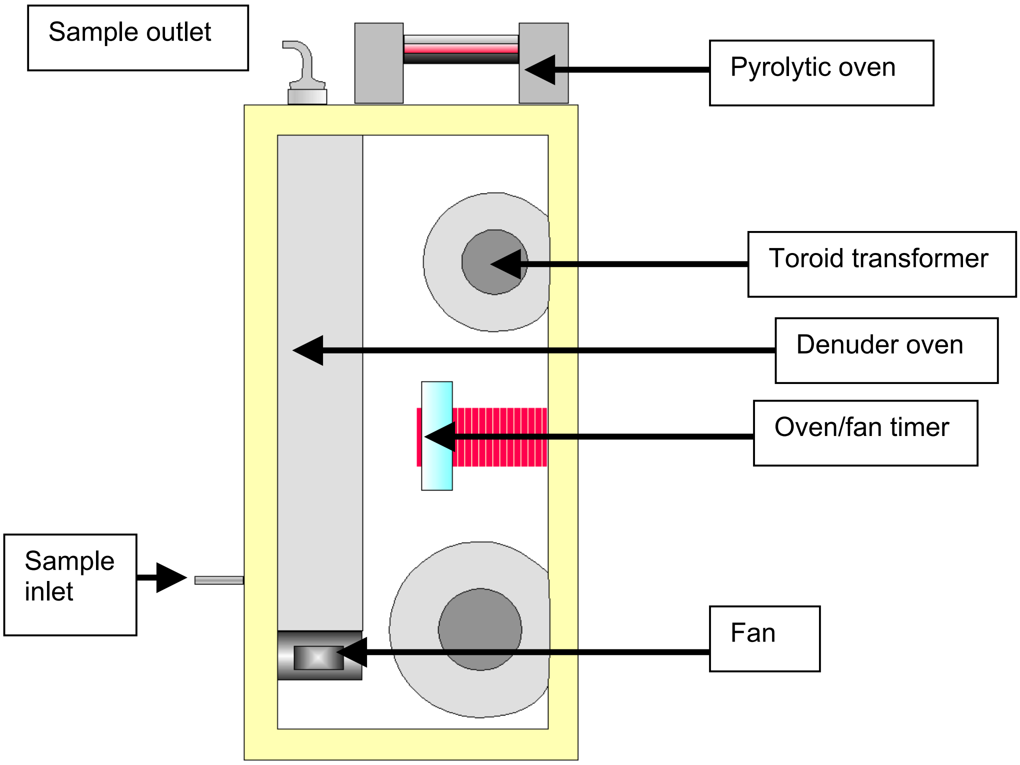

Figure 13: The desorption system.

The measures of the system in Figure 13 was: height 48 cm, width 24 cm and depth about 15 cm. The system had two transformers. One supplying power to the denuder oven, and the other to the pyrolytic oven intended for the pyrolysis tube. On the pyrolytic oven the heating coil was placed directly onto a quarts tube (where the pyrolysis tube was put inside), and was held at a temperature of 900°C during operations.

Laying a heater coil on a quarts tube, and a ceramic insulation textile on the outside made the denuder oven. The oven was fitted into an aluminium profile and placed inside the enclosure. A blower fan was placed under the bottom of the denuder oven.

A small timer device made the denuder oven transformer run at its maximum output for 11 min, to obtain the required desorption window (denuder temperature > 450°C). When the transformer was turned off, the timer started the blower fan to cool down the denuder and the oven. The only venting was through the quarts tube. The power surge was so high that a voltage stabiliser had to be utilised to prevent the mains power distribution fuses from blowing when the system was turned on. Specifications of materials used in this oven system and in the modified version, can be viewed in Table 2.

Table 2: Specifications of denuder oven system parts.

Item	Part no.	Specs.	Manufacturer	Address
Transformer	56-139-30	230V to 2x 24 V 600 VA 48 to 60 Hz	Transductor International AB	
Transformer	56-137-32	230V to 2x 24 V 250 VA 48 to 60 Hz	Transductor International AB	
Timer	H3DE-M2		Omron Europe B.V.	Hoofddorp, The Netherlands
Solid State Relay	V23100-S0302-A225		Siemens	
Delay circuit	n/a	Tailor made	NILU	N-2027, Kjeller, Norway
Insulation version 1; ceramic textile		Maximum 1200 degrees	Keranova AB	Sweden
Insulation version 2;	MB700	Firefly Millboard, 2x4mm	Tenmat Ltd.	Manchester, M17 1RU, England
Quartz tube for denuder tube		30x27x270mm	Quartz Glas Technik Gmbh & Co	Bad Hartzburg, Germany
Quartz tube for pyrolytic oven		18x15x80mm		
Oven case, square aluminium profile		80x72x380mm	Hydro Aluminium	
Oven top and bottom, aluminium bolt	n/a	Machined in house	NILU	
Glass, bent adapter		Duran glass	Lentz Laborglas	Wertheim, Germany
PID-controller for denuder oven	N6101/ Z2220/00		West Instruments	Brighton, BN2 4JU, England
Heating coil for pyrolytic oven	Nikrothal 80	1.1 ohm	Kanthal	
Heating coil for denuder oven	Nikrothal 80	1.1 ohm first version, then 0.6 ohm	Kanthal	
Thermocouple element K	76-808-61	-50°C to +1150°C		
Denuder oven fan	8556N	50 m3/h at 2800 RPM	Papst	D-78106 St. Georgen, Germany

3.3.4 *Analysis system*

When a sample is analysed, the system is configured as visualized in Figure 14. The gas bottle is at all times open, driving zero air out through the Teflon tee pressure relief unit. When the pump in the GARDIS starts up, the pre decided flow of air is pulled through the system. Excess zero air is released through the Teflon tee. As mentioned, the “normal” sample introduction flow on the monitor is 1 L/min. To achieve the desired 200 ml/min, a small glass capillary tube on the back of the monitor restricts the pump.

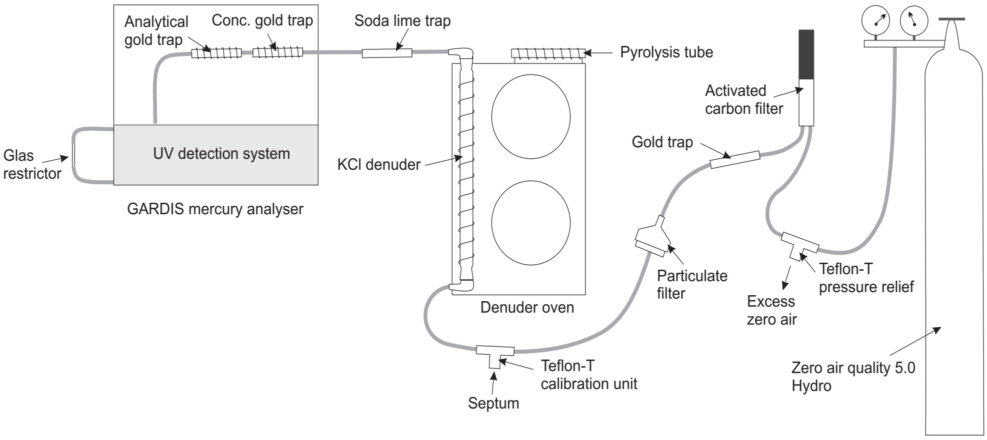

Figure 14: The configuration of the analytical system. In some cases the soda lime trap is connected, in others the pyrolysis tube is coupled instead. Occasionally none of them are connected and the KCl denuder is linked directly to the GARDIS gas inlet.

Zero air is pulled from the bottle through an activated carbon filter, a gold trap and a particulate filter to remove humidity, mercury and particles, before it passes the calibration injection unit. The air goes through the sample denuder, kept at 500°C, and “collects” the elemental mercury released from the denuder. Before entering the GARDIS, the sample moves either through the pyrolysis tube, held at 900°C, or through the soda lime trap (which is not heated). The pyrolysis tube consists of a 15 cm long quarts tube with i.d. 5 mm and o.d. 7 mm, filled with small quarts beads about 1 mm in diameter. The soda lime trap consists of the same tube but now filled with soda lime pellets. The tube and the trap are both supposed to remove organic pollutants. In some cases the denuder can be connected directly to the GARDIS gas inlet, both tube and trap are disconnected. The mercury sample is collected on the concentrating gold trap in the GARDIS, released when the trap is heated to 700°C, re-trapped on the analytical trap and released again when this trap is heated to 700°C. When the GARDIS is used to monitor TGM concentrations in ambient air, the concentrating gold trap will protect the analytical gold trap from pollutants, as well as act as an extra concentrating step. Working with GDM analysis, one trap would be sufficient to achieve quantification. A 10 ml/min flow of zero air then leads the sample into the detector described in detail in section 3.3.2. The amount of mercury in the sample is quantified and displayed on a connected computer.

3.4 Descriptions of system parts

All available specifications of parts, pieces and chemicals, are listed in Appendix 2.

4 Procedures and experiments

All specifications of materials and chemicals described in this chapter are listed in Appendix 2.

4.1 Procedures

The following procedures are common for most experiments and field studies. Deviations are described for each single experiment.

4.1.1 Cleaning of quarts, glass and Teflon

In order to extract traces of mercury polluting the materials used in experiments, a Br-Cl solution is utilized. The solution is made by the following procedure. Potassium bromate ($KBrO_3$) is placed in a porcelain dish and heated for 24 hours in a ceramic oven at 250 ± 20. Likewise, Potassium bromide (KBr) is heated at 300 ± 20°C for 24 hours. 11.0 g $KBrO_3$ and 15.0 g KBr are added to 200 ml ultra clean (Milli-Q plus) water. The mixture is blended (by a magnet stirrer) for 1 hour before 800 ml concentrated HCl is added some at the time. This procedure must be undertaken in a ventilation hood due to the formation of toxic halogen gases (Cl_2, Br_2) during the process. Before use, and between experiments, all quarts, glass and Teflon parts are soaked in this solution for at least 24 hours. The parts are then rinsed in Milli-Q water five times before they are dried by heating in a ceramic oven at 100±20°C. Cleaned parts are kept in air-tight bags until they are used.

4.1.2 Coating the denuders

This procedure is conducted in clean room facilities to avoid large contaminations from the surrounding air. The system in Figure 15 is placed in a ventilation hood to prevent the operator from inhaling the methanol vapour. The denuders are soaked in a Br-Cl solution for at least 24 hours, rinsed thoroughly in distilled water, minimum five times, and dried before coating (see above). Methanol is filled into a 100 ml Pyrex beaker and heated on a hot plate. When the methanol reaches the boiling point, KCl salt is added until the solution is saturated. The heat is turned off and the solution is allowed to cool for about 30 s before it is pulled up into the denuder (using a peleus balloon), all the way to the top of the active area. The solution is kept in this position for about 10 min in order to cool and crystallise KCl onto the walls, before it is slowly lowered down to the beaker again. The denuder is allowed to dry for about five minutes while the solution is stirred and boiled again. The procedure is repeated three times. The third time the solution is kept in the denuder for 20 min, so that the walls will be covered as much as possible in crystals. To facilitate drying, the denuders are placed in an upright position and left in the ventilation hood for at least 12 hours. Crystals situated outside the active area on the denuder are then removed with a paper tissue drenched in Milli-Q water.

The procedure above was established after the tests showing that a thicker layer of coating might increase the sampling efficiency of the denuders. See breakthrough tests in section 6.1.10. Prior to this point the procedure was identical, except from the times the solution was kept in the denuder. It was then 3-3-5 minutes instead of 10-10-20.

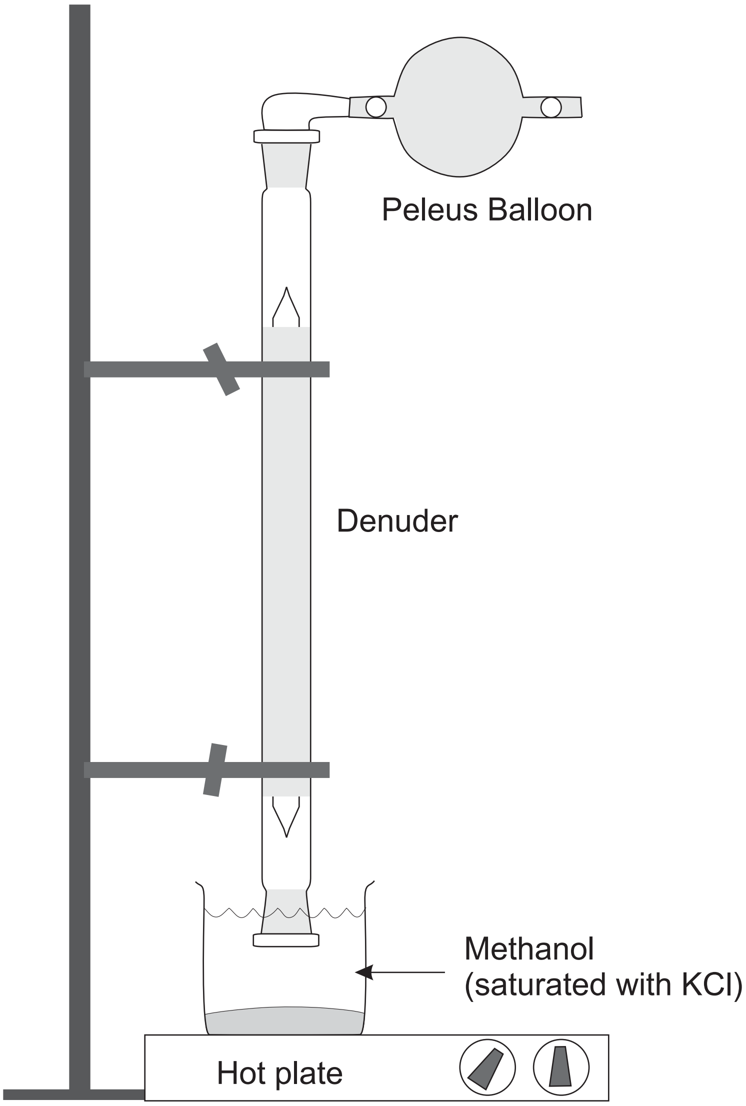

Figure 15: Set up for coating procedure.

4.1.3 Analysis

The GARDIS monitor is turned on at least one hour prior to use in order to heat the lamp. To quantify the amount of mercury trapped on a denuder, it is placed in the denuder oven and connected to the system as described in section 3.3.4. The GARDIS monitor is set to pull zero air from the gas bottle, through the system and denuder, and in to the monitor for 15 min (the sample introduction time). The introduction flow is set to 200 ml/min. When the monitor starts pulling air, the operator presses the start button on the denuder oven. The denuder will then be heated to 500°C and kept at that temperature until the introduction of the sample is over. As the monitor starts quantifying the mercury sample (see section 3.3), a fan in the denuder oven starts off cooling the oven and denuder. If additional measurements are required the procedure is repeated after the result has been displayed on the computer. The displayed value is based on the peak height. The denuder should not be removed from the system before the temperature has descended to 100°C. At higher temperatures the denuder might be stuck because of the material's expansion. Attempts to take the denuder out may then cause breakage to the system parts.

4.1.4 Preparation of denuders

Mercury contaminations from quarts, methanol and KCl on the newly coated denuders, are removed by thermal desorption. The denuder is placed in the denuder oven in the analysis system. It is heated, and the amount of mercury released is quantified on the GARDIS monitor in the same way as an ordinary sample (see section 4.1.3). The process is repeated until mercury is virtually no longer released. After removing the denuder from the system it is left to cool down on a bench for about 20 min. Hollow glass stoppers and plastic clips are used to close the denuder properly in both ends, before it is placed in two airtight bags for storage.

4.1.5 Calibration

To perform calibrations, the denuder oven in Figure 14 is disconnected and the Teflon tee injection port is coupled, with tubing, directly to the GARDIS inlet. The system is run as if a sample was present, but without using the denuder oven (see section 4.1.3). Calibrations can be performed with either the pyrolysis tube or the soda lime trap connected, or neither. The mercury background signal from the analysis and introduction system is measured. Several consecutive measurements are performed to establish a stable background value. A gas-tight syringe is used to take out a known amount of mercury from a reservoir of air, saturated with Hg (see section 3.3.1). Introduction time is set to 15 min, and as the monitor starts pulling air through the system, the saturated air in the syringe is injected through the septum in the calibration port. The established background value is subtracted from the result displayed on the GARDIS before the percentage magnitude of the displayed signal, relative to the injected amount (recovery), is calculated. The displayed signals are based on peak heights.

The value displayed on the computer for a signal of certain magnitude, relies on the calibration constant set on the GARDIS. About once a month, or between sampling campaigns, a full calibration is performed and the calibration constant on the GARDIS is adjusted. Between three and five measurements are carried out injecting the same amount of mercury. A mean value of the measured results is calculated and the established background subtracted. The resulting value is compared to the injected amount of Hg, and the calibration constant is adjusted to make the monitor display a result as close to the true value as possible. The constant is adjusted until the signal corresponds to the injected amount. A full description of the calculations made, is showed in A.1.2.

Daily calibrations can be performed in two ways. If the response of the detector is linear over a large area, the calibration can be executed in the same way as when adjusting the calibration constant (see above). Instead of adjusting the constant according to the calculated relative magnitudes, the measured sample values are increased (or decreased) directly. An example exists in A.1.3. If the detector, on the other hand, does not give a linear response, a standard curve has to be made. Between three and five injections of different amounts of Hg are performed and measured. The amounts injected are chosen to cover the area where the sample value is expected to be. From each of the results the background value is subtracted and the percentage magnitude of the displayed signal, relative to the injected amount is calculated. These relative magnitudes are plotted against the displayed values, giving a standard curve. When the amount of mercury on a sample denuder is measured, the result is subtracted the background value, and a "true" value is calculated by adjusting the value according to the standard curve. A.1.3 gives an example of such a calibration.

4.1.6 Sampling blanks

To discover the background values obtained through the whole process of sampling and analysing, sample blanks are measured. The sample blanks are denuders treated exactly the same way as the samples. The initial mercury signals from the blanks are measured and noted before "sampling" together with the sample denuders. Before the sample denuders are put in the sampling box, the blanks are connected as described in section 3.2.3, taken out again, plugged with hollow glass stoppers and plastic clamps and placed next to the sample denuders during the whole sample period. They are also analysed together with the samples.

4.2 Experiments

4.2.1 Testing the stability of the background from the analytical system

To test the stability of the background values from the analytical system, several consecutive measurements were performed. The system was put up like in Figure 14, except that the tubing coming out of the particulate filter was connected directly to the GARDIS inlet. The denuder oven, pyrolysis tube and soda lime trap were not connected. The introduction time was set to 600 s, introduction flow was 200 ml/min, chopper speed in the detector was 220 rounds/s, and twenty-seven measurements where made. After recording the twenty-seven results their mean value, minimum, maximum, standard deviation and relative standard deviation where calculated. See results section 6.1.1.

The same experiment was then repeated but with an introduction time of 720 s, flow 200 ml/min, chopper speed in the detector 250 rounds/s. Twenty-seven measurements were made. The same parameters as above were calculated. See results in section 6.1.1.

4.2.2 Initial calibration of the mercury monitor

The GARDIS monitor was calibrated according to the procedure described in section 4.1.5. The pyrolysis tube or the soda lime trap was not connected. The calibration constant on the GARDIS was initially 250. Introduction time was set to 600 s and introduction flow was 200 ml/min. Eleven doses of about 180–200 pg of mercury were injected and measured successively. The background values from the system were measured between each injection, and the mean of the background value before and after an injection measurement was subtracted from the displayed injection value. Deviation from true value was calculated for each result and statistics performed on the whole set of data. A.1.2 gives an example of the calculations.

After adjusting the calibration constant to 325 according to the previous results, five new injections and measurements were performed. Conditions and calculations were identical to the above.

Four different amounts of mercury were then injected and measured under the same conditions. Plotting the measured values as a function if the injected amounts made a standard curve. See results in section 6.1.2.

4.2.3 Checking the denuder coating

A denuder was coated according to the procedure in 4.1.2. Microscopy pictures were taken of the denuder and the coating, and the pictures were sent to Dr. Xinbin Feng at State Key Laboratory of Environmental Geochemistry, Chinese Academy of Sciences, Guiyang, P.R China[49], to be evaluated. Pictures and discussion in section 6.1.3.

4.2.4 Introduction of the pyrolysis tube

The pyrolysis tube was connected between the injection port and the GARDIS monitor during calibrations, and between denuder oven/denuder and GARDIS during analysis. The temperature in the tube was at all times held at 900°C.

At first a new quarts tube filled with 1 mm pieces of the same quarts was connected. The tube and pieces had not been cleaned in Br-Cl solution prior to use. Injections of mercury and measurements were performed as described in section 4.1.5. Introduction time was 900 s, introduction flow 200 ml/min and the calibration constant 325. Results in Table 8.

Pyrolysis tube and beads were soaked in Br-Cl solution for 48 hours and rinsed in ultra clean Milli-Q water five times. The empty tube (no beads) was connected and injections performed as above. See results Table 9.

The tube was filled with the cleaned quarts beads and re-connected. Injections performed as above. See results Table 10.

Experiments concerning the pyrolysis tube were also performed during a field study on the Mediterranean Sea. Conditions during the measurements on the Mediterranean Cruise are described in section 5.2.

4.2.5 The impact of changing the introduction times

The precision of the GARDIS measurements at different introduction times was tested by measuring the mercury concentration in the laboratory air. The monitor, not connected to the rest of the system, was set to sample and measure the air three times at each introduction time. Six different introduction times were tested out, the longest being 300 s, and the shortest 30 s. The measurements were performed during the night. The results can be viewed in results Table 11.

4.2.6 Memory effects

A test was performed to reveal possible memory effects in the monitor using very short sampling times (small sample volumes). The GARDIS was disconnected from the rest of the system in Figure 14. A particulate filter was coupled to the monitor inlet, and a Teflon tee calibration port connected to the filter. Both connections were made by the use of Teflon and viton tubing. Sample introduction time was set to 60 s, the introduction flow was 100 ml/min and the calibration constant 289. At first the background from the laboratory, filter and Teflon tee was established. Then a known amount of mercury was injected into the calibration port while the GARDIS was pulling laboratory air, and the result measured on the monitor. Subsequently several successive measurements were performed without injecting more mercury. Results in section 6.1.5.

In the following experiments the conditions were identical to those above. Modifications were only performed to tubing and filter connected to the GARDIS.

4.2.7 Modifications on the denuder oven

The initial denuder oven system described in section 3.3.3, was put through a test to establish a temperature curve for the denuder during analysis. A denuder was placed in the oven with a thermocouple sensor inside. The heating was turned on, and the temperature inside the denuder was recorded every 15 seconds throughout the whole process. The resulting curve can be viewed in Figure 23 in section 6.1.7.

Several modifications were then performed at the instrument laboratory at NILU, leading to the design in Figure 16 and Figure 17. To compare to former design, see Figure 12 and Figure 13.

The pyrolysis oven was left out because of changes in the analysis procedure. A delay circuit with semiconductor relay was introduced. The semiconductor relay does the switching exactly when the mains voltage cycles through zero, and thus avoids the power surge – a kind of “soft start”. A PID-controller and a temperature sensor were introduced to the denuder oven. The PID-controller output controls the denuder oven relay. This relay is identical to the delay circuit. The heating coil was exchanged for another with lower resistance, and the insulation was moved from outside the heater coil to the inside of the aluminium profile walls. The fan was changed to one with higher capacity. An intake giving the option to connect an air venting tube to the fan was constructed. This connection made it possible to bring in cold air from outside the laboratory. Extra holes were also drilled on the top of the oven base.

A temperature curve for the denuder was established by the same procedure as for the initial oven (see above).

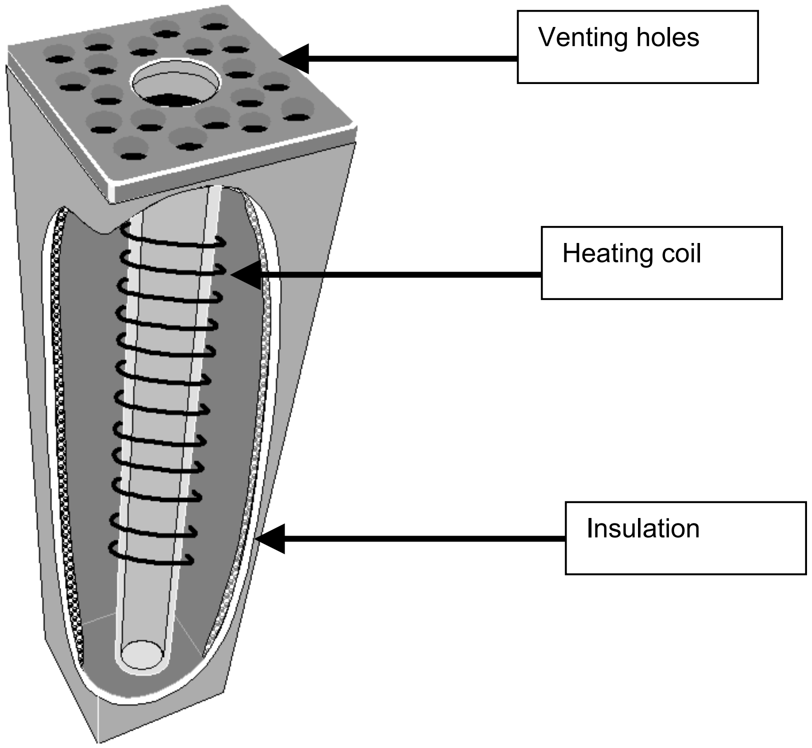

Figure 16: The interior of the modified denuder oven (compare Figure 12).

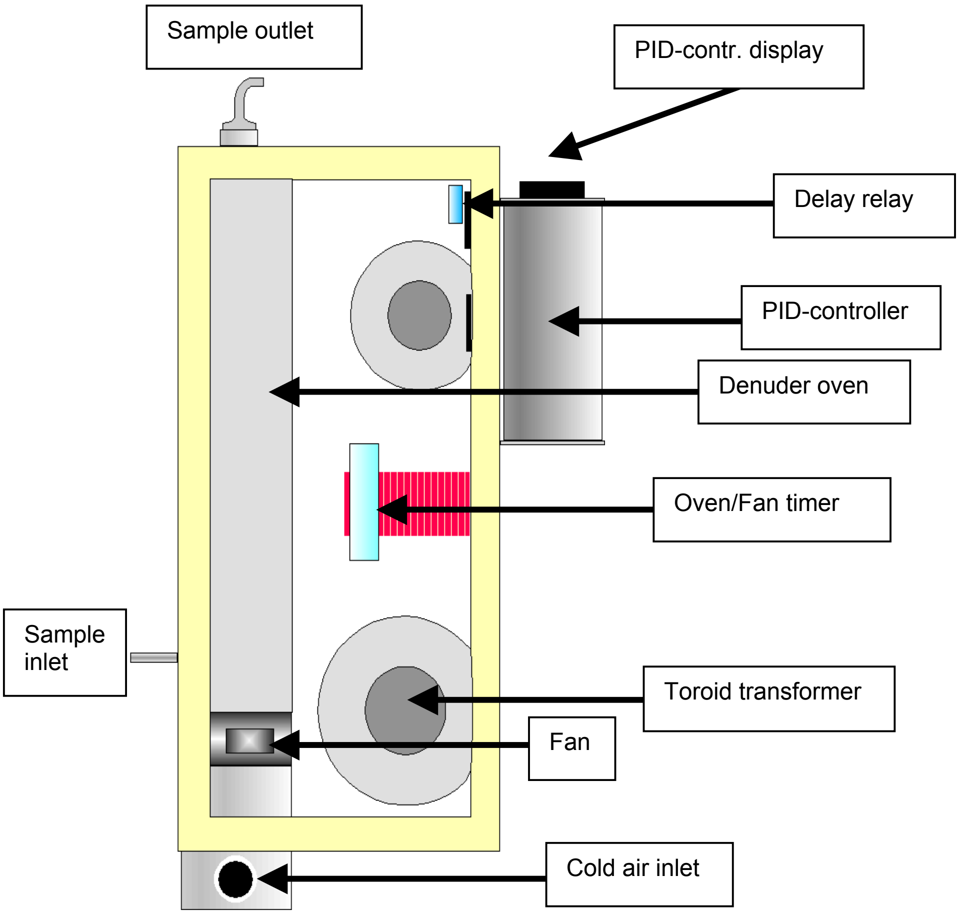

Figure 17: The modified desorption system (compare Figure 13).

4.2.8 The influence of introduction time on signal magnitude

Two identical experiments were performed, except for the sample introduction time being changed. The system was set up as described in section 4.1.5, and the test was performed both with and without the pyrolysis tube connected. In the first experiment the sample introduction time was 120 s, introduction flow was 200 ml/min and the calibration constant 491. The pyrolysis tube was not connected. Four different amounts of mercury were injected and background from the system was subtracted from the displayed values. The results' relative magnitude compared to the injected amounts was plotted as a function of injected amounts.

The second experiment was identical except for the sample introduction time now being increased to 900 s. Results are shown in Figure 25 section 6.1.8.

The experiment was repeated with the pyrolysis tube connected in the system.

4.2.9 Introduction of the soda lime trap

A small quarts tube filled with soda lime pellets (see section 3.3.4) was placed in the analysis system. The soda lime trap replaced the pyrolysis tube and was put between calibration port and GARDIS inlet during calibration, and between denuder/denuder oven and GARDIS inlet during sample analysis and cleaning. Working with the cleaning tests and GDM measurements, the system was calibrated on daily basis according to the procedure in section 4.1.5.

Standard injections with and without the soda lime trap:
At first the calibration port was connected directly, with Teflon tubing, to the GARDIS inlet. Sample introduction time was 900 s, introduction flow was 200 ml/min and the calibration constant was 450. Three different amounts of mercury were injected and quantified. After subtracting the system background, the measured results were plotted against the injected values (see Figure 26 in section 6.1.9.).

The soda lime trap was then connected and the same procedure was repeated. The measured results were plotted against injected amounts in the same figure as above. See results in section 6.1.9.

Thermal cleaning of denuders:
Two tests were performed regarding cleaning of denuders. The cleaning was in both cases performed according to the procedure described in 4.1.4.

The first test was performed without the soda lime trap connected to the system. The denuder oven was modified at this point. The sample introduction time was 900 s, the sampling flow200 ml/min and the calibration constant was 450. An “unclean“ denuder was placed in the oven. Repeated desorptions and measurements were performed until the denuder was almost clean. See results in section 6.1.8.

The second test was identical except that the soda lime trap was now connected to the system. See results in section 6.1.8.

Measured GDM concentrations in laboratory air with and without soda lime trap connected:
The GDM concentrations measured in the laboratory air when the soda lime trap was not connected, were compared to the results after connecting the trap. In both cases the sample introduction time was 900 s, the introduction flow was 200 ml/min and the calibration constant 450. The sampling conditions are described in section 4.2.10. See also results in section 6.1.10.

4.2.10 Breakthrough testing

All of the breakthrough tests where performed in the laboratory, sampling laboratory air. A system calibration/standard curve, was completed every morning according to the procedure described in section 4.1.5. The sampling efficiency of the denuders was tested by connecting two denuders in series, using bent glass adapters, viton tubing and plastic clamps. See the set up in Figure 18 below. The denuder placed in the back was coupled to the pump the same way. By turning on the pump, air was pulled through both of the denuders. After pulling air through for the required amount of time, the pumps where switched off. The total amount of air pulled through could be read on the gas-clock on the pump, counting litres. The flow could then be calculated. After finishing the sampling the denuders were disconnected from each other, and plugged with hollow glass stoppers and plastic clamps until they were analysed according to the procedure described in section 4.1.3. The denuder oven was modified at this point. The amount of GDM on both denuders was measured and total amount, concentration and distribution were calculated in section 6.1.10.

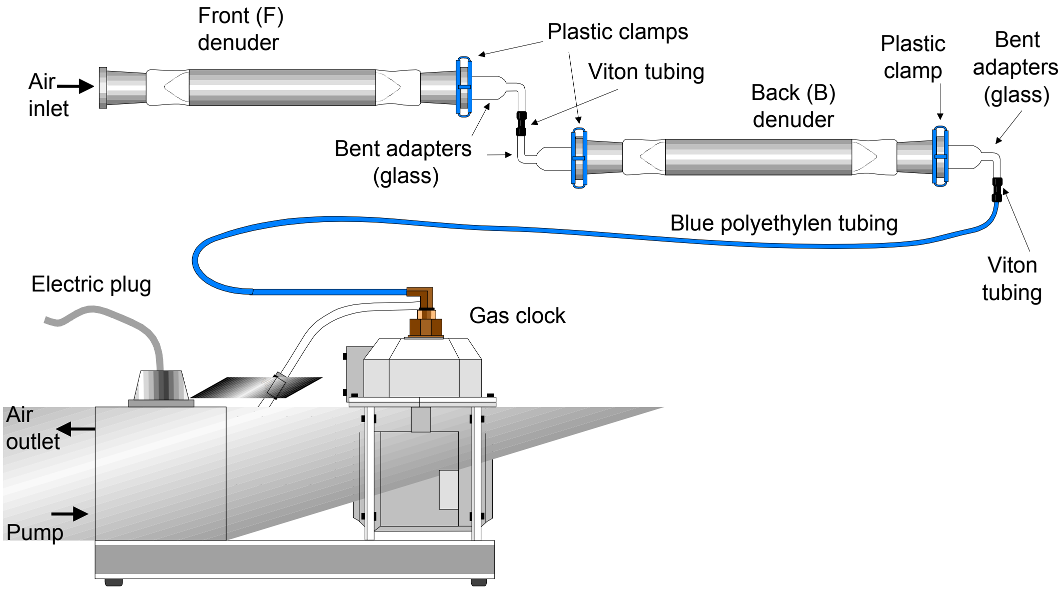

Figure 18: Sampling set up for breakthrough testing. In lower right corner a front view of the pump.

The first experiment, mentioned above in section 4.2.9, included four tests as described above. Exact sampling flow and volume for each test can be viewed in Table 15 section 6.1.10. The same table also includes measured GDM amounts and calculated results. The sampling time was approximately 24 hours in all these tests. The analysis were carried out according to the procedure in section 4.1.3.

The denuders were connected directly to the GARDIS inlet with bent glass adapters and viton, Teflon and silicon tubing. Neither the pyrolysis tube nor the soda lime trap was a part of the system. Sample introduction time was 900 s, introduction flow was 200 ml/min and the calibration constant 450.

One identical test was performed were the soda lime trap was connected. See Table 16.

All conditions were identical in the test presented in Table 17, except that denuder 9, the one in front, had been recoated before use.

Table 18 presents two tests in which the sampling flow was increased considerably. All other conditions were identical to the previously described. Denuder number 9 was still the only recoated one.

The last breakthrough test was performed with the high sampling flow (about 6 L/min) and the sampling time was reduced from about 24 hours to less than six hours. Results are presented in Table 19.

4.2.11 Blank samples and the limit of detection

In order to determine the limit of detection for the analysis system, 10 consecutive background measurements were performed in the laboratory. Denuder oven, calibration port and pyrolysis tube were disconnected, but the soda lime trap was connected. System set up as described in section 3.3.4. Sample introduction time was 900 s, the introduction flow was 200 ml/min and the calibration constant was 450. Using the measured background values from the system, the average, the minimum and maximum value, standard deviation and limit of detection were calculated. See the results in Table 20.

To find the limit of detection for the whole sampling and analysis process, five blank samples were measured. The samples were obtained as follows. Five denuders were cleaned in addition to the ones intended for sampling. The cleaning procedures were identical for sample denuders and blanks. Sample introduction time were 900 s, introduction flow 200 ml/min and the calibration constant 450. Each of the five blank denuders was coupled to the pump the same way as the samples. They were then disconnected and plugged with hollow glass stoppers and plastic clamps. After connecting the sample denuders to the pump, the denuder blanks were placed next to the samples and left there for as long as the sampling took place (about 24 hours). The sampling took place in the laboratory. The blanks were then analysed together with the samples under the same conditions as above. From the measured values the minimum and maximum value, standard deviation and limit of detection was calculated. See the results in Table 21, section 6.1.11. The daily calibration as described in section 4.1.5, was executed early in the morning.

The experiment was repeated working out in the field at the Zeppelin station on Svalbard. Following the procedure in section 4.1.6 and under the conditions described for the Zeppelin study in section 5.1.2, 10 background measurements were performed to establish the limit of detection for the introduction and analytical system. 10 sample blanks were analysed to determine the limit of detection for the whole system. Calculated results in Table 22 and Table 23, section 6.1.11.

Under identical conditions, the GARDIS monitor was exchanged for a Tekran monitor. 10 background measurements were performed, and calculations made as above. Results in Table 24 section 6.1.11.

5 Field studies

5.1 Studying the arctic environment in Ny-Ålesund, Svalbard

The purpose of these studies was to quantify the GDM concentrations during the Arctic depletion episodes of elemental mercury. The measurements were performed at the Zeppelin station at Ny-Ålesund, Svalbard in the Norwegian Arctic, during April and May 2000 and 2001. The map in Figure 19 shows Svalbard. The following description is drawn from an article by Sverre Solberg et al. in 1997[43].

Ny-Ålesund is a small settlement near the sea level on the western coast of Spitsbergen, located on the south side of Kongsfjorden. The settlement is situated 78° 54’ N and 11° 52’ E. The site is surrounded by steep mountains with tops about 5-600 m a.s.l., to the south of Kongsfjorden.

Figure 19: Map of Svalbard. Ny-Ålesund is situated at 78°54’N and 11°52’E.

The research station on the Zeppelin Mountain has an altitude of 474 m a.s.l., and is accessible from Ny-Ålesund by cable car. The station is located on a mountain ridge, with steep down hills to north and south, and with higher mountain peaks to the west and east. The mountain station was established to minimize the influence from local pollution. Shallow surface inversions are common in the Arctic, and measurements at Ny-Ålesund might therefore occasionally be exposed to the small anthropogenic emissions from the nearby settlement, trapped in the inversion layer. This contribution is thought to be negligible at the Zeppelin station.

A high resolution, automatic TGM monitor (Tekran Model 2537A), based on AFS detection, was installed at the Zeppelin station by the NILU in February 2000. The monitor measures the TGM concentration in the ambient air every 5 minutes.

At the Zeppelin station the sampling line and the analysis system was arranged in the same way as described in sections 3.2.3 and 3.3.4. In analysis performed in the spring of 2000, the unmodified version of the denuder oven was utilised. In the spring of 2001, the modified oven was used. The sampling box was placed on the outside wall on the station’s eastern side, about 1.5 meters above a metal grating floor.

5.1.1 Studies at Ny-Ålesund, Svalbard spring 2000

Denuders were coated according to the “old” procedure described in section 4.1.2. Measurements were performed on a daily basis and the sampling time was about 24 hours. Two parallel samples were taken on the 29.04, 30.04 and 04.05. All other days only one result was measured. No blank samples were analysed. No standard curves were made, but each day, except from 10.05, three or four different mercury amounts were injected. The displayed mercury values did not deviate from the injected amounts by more than 20%. Accordingly, the measured values were not modified. Before analysis of the samples from 10.05, the displayed mercury values deviated very much from the injected amounts. A full standard curve was made, and the measured results adjusted according to this. The calculations are described in Appendix 1. Each day the denuder/denuders were thermally cleaned and the last measured mercury signal was recorded. After cooling down, the denuder/denuders were placed in the sampling box as described in section 3.2.3. The time and the initial value on the gas clocks were recorded as the pumps were switched on and of. Calculation of the air volume is described in Appendix 1. The oven inside the sampling box was set to keep the temperature at about 40°C, and the sampling flow approximately 3.5 L/min. Immediately after sampling, the denuders were analysed according to section 4.1.3, and another set of cleaned denuders were put into the box. During analysis the sample introduction time was 900 s, the introduction flow 200 ml/min and the calibration constant 344.

The results are presented in section 6.2.1. The TGM concentrations presented are obtained by averaging all the five-minute measurements from the Tekran monitor over the same interval of time, as the GDM samples were collected. An example of a series of Tekran TGM measurements can be viewed in Appendix 8.

5.1.2 Studies at Ny-Ålesund, Svalbard spring 2001

Denuders were coated according to the “new” procedure described in section 4.1.2. Measurements were performed on a daily basis and the sampling time was about 5-6 hours. Sampling normally took place between 10 am and 4 pm. Two parallel samples and one blank sample were collected every day. In the morning the two denuders for sampling and the one for blank measurements were thermally cleaned and the last measured mercury signal was recorded. The modified version of the denuder was utilised. After cooling down, all three denuders were placed in the sampling box described in section 3.2.1. The blank denuder was treated as described in section 4.1.6. The time and the value on the gas clocks were recorded as the pumps were switched on and off. See in calculations in Appendix 1 about how to find the air volume. The oven inside the sampling box was set to keep a temperature of about 40°C, but was apparently not able to do so. The temperature in the box during sampling was therefore not known. The sampling flow was around 6 L/min. In the middle of every day a standard curve was made as illustrated in Appendix 1. Immediately after sampling the three denuders were analysed (see section 4.1.3). During analysis the sample introduction time was 900 s, the introduction flow 200 ml/min and the calibration constant 450.

GDM amounts and concentrations were calculated in accordance with Appendix 1 and the results are found in 6.2.1. The TGM concentrations presented are obtained by averaging all the five-minute measurements from the Tekran monitor over the same interval of time as the GDM samples were collected. An example of a series of Tekran TGM measurements can be viewed in Appendix 8.

5.2 The Mediterranean research cruise

An invitation was received from the Italian National Research Council, to participate in an oceanographic cruise on the Mediterranean Sea for two weeks in July/August 2000. The cruise was part of a pilot study, which was aimed to assess the role of air-sea interface in the cycle of atmospheric mercury over the Mediterranean Sea. The focus was on mercury, but other pollutants like NO_x, SO_2, O_3 and metals were also determined. Enclosed in the appendix is the whole cruise description received from the Italian National Research Council[50].

The sampling box was placed on a rail on the upper deck. The pumps that were actually intended only for indoor uses had to be placed under a plastic cover outside. The analytical laboratory was situated in a room on the lower deck. The analytical system was put up as described in section 3.3.4. The denuder oven was not modified at this point. All the parts of the analysis system had to be fastened with screws or ropes because of potential heavy movement at sea. The air in the laboratory was 2-3 times more polluted than in the laboratories usually employed (8-9 pg/l). The air condition system was dysfunctional so the doors had to be kept open at all times. This resulted in major temperature variations during the day in addition to all the fumes that entered the room from outside. The electricity was guarantied by the crew to be stable, but the sound of the generators indicated large variations also here. The signal magnitude from the injected standards deviated largely from each other every day.

Measurements were performed on daily basis and the sampling time was about 24 hours (same as for the Italian group also measuring GDM). The temperature control on the heater in the box was set to 30°C to match the conditions in the Italian sampler. The sampling flow was about 2.5 l/min. Two sample parallels were taken every day. No blank samples were analysed. Most of the days several injections of mercury were performed. Standard introduction time was 180 s. Flow and calibration constant were the same as for the analysis. Even though the signals deviated largely from each other, an approximation was made to the mean deviation from injected value, and the sample results were corrected according to this. As shown in Table 27. The pyrolysis tube was connected in the analysis system the first days of the cruise. After that, some measurements were made with the tube connected and some without. The last three days the tube was disconnected. After performing standard injections in the morning, two denuders were cleaned, measured and put into the sampling box as illustrated in section 3.2.3. Immediately after sampling, the denuders were analysed according to section 4.1.3, and another set of cleaned denuders were put into the box. Throughout the analysis the sample introduction time was 900 s, the introduction flow 200 ml/min and the calibration constant 350. The last two days pump number 5 did not work properly, because it was drowned in a heavy rainfall, and the concentrations of mercury detected on denuders connected to this pump were disregarded.

Parameters like wind speed, humidity and temperature were continuously measured by instruments onboard the ship.

6 Results and discussion

6.1 Experiments

6.1.1 The stability of the background from the analytical system

Some optimising tests concerning the analysis of denuders had previously been performed by a research group (using a similar system) at “Chalmers University of Technology”[48]. The ideal sample introduction flow was found to be 200 ml/min. At this flow the gold traps in the detection systems would collect close to 100% of the elemental mercury from the carrier gas (at least when concerning such small amounts of mercury as in these experiments). They also discovered that after heating the denuder at 450 - 500°C for 10 minutes, no more mercury was released from the surface. The desorption efficiency was then close to 100%. According to this, the sample introduction time (and denuder heating time) was initially set to 600 s. Performing tests, it appeared that the denuder oven needed several minutes to reach the 450°C limit. The sample introduction time was therefore first increased to 720 s, and later to 900 s to achieve the desired desorption time. This was the reason why the following two experiments were performed with different sample introduction times. Further descriptions of the experiment conditions can be found in section 4.2.1.

The system background is the magnitude of the mercury signal created by carrier gas, introduction system and detector, when no sample or standard is present. Several consecutive measurements were made to investigate the stability of this signal. The results are presented in Table 3.

Table 3: Initial stability parameters for background measurements (conditions described in section4.2.1).

Before	
average(pg)	2.9
min.(pg)	0.6
max.(pg)	5.8
st.dev(pg)	1.3
rel.st.dev	43.4%
count	27

A relative standard deviation of 43.4%, was a severe problem. Several identical experiments were performed after checking the whole system for leakages and changing different system parts. None of the adjustments had any effect on the deviation. After consulting the GARDIS manufacturer, the chopper speed in the detector was increased from 220 rounds/s to 250 rounds/s. A new experiment was performed and the results are presented in Table 4.

Table 4: Stability parameters for background measurements after changing the chopper speed from 220 round/s to 250 rounds/s (conditions described in section 4.2.1).

After	
average(pg)	1.7
min.(pg)	1.4
max.(pg)	2.2
st.dev(pg)	0.2
rel.st.dev	12.9%
count	26

The relative standard deviation of the measurements was significantly improved from 43.4% to 12.9%.

The chopper modulation is intended for the light intensity comparison between the sampling and reference cell. Even the initial chopper speed of 220 rounds/s (15-20 Hz), should yield by far enough light comparisons per second, since the baseline finally is drawn with a time resolution of one second. The manufacturer could, however, inform that low frequencies of chopper rotation sometimes tended to interfere with other common frequencies, such as the diaphragm pump rotation. Occasionally, it might therefore be useful to have a higher chopper rotation speed. An increase of the chopper speed could lead to more wear and tear of the analyser. It was recommended not to change the speed without consulting the manufacturer. Since the manufacturer did not recommend any additional increase of the chopper speed, no further tests were performed.

6.1.2 Initial calibration of the mercury monitor

Before using the GARDIS to quantify samples, a thorough calibration of the monitor had to be made. The calibration was carried out according to the procedure in section 4.1.5 and description in section 4.2.2. An example of the kind of calculations used, is presented in Appendix 1. The size of the displayed signals was calculated relative to the injected amount of mercury. Initially the signals' magnitude was only 76.4% ±2.7% of injected amount, as shown in Table 5.

Table 5: Initial result of standard injections. The average result is given as the displayed signal magnitude relative to the injected amount of mercury (average recovery) (conditions described in section4.2.2).

Before	
Av.result.	76.4 %
St.dev	2.7 %
Rel.st.dev	3.5 %
Count	11

To increase the displayed signal to the same magnitude as the injected amounts, the calibration constant was raised from 250 to 325, and a new set of mercury doses were injected. Results in table 6.

Table 6: Results of standard injections after adjusting the calibration constant on the GARDIS. The average result is given as the displayed signal magnitude relative to the injected amount of mercury (conditions described in section4.2.2).

After	
Av.result	101.6 %
St.dev	2.2 %
Rel.st.dev	2.2 %
Count	5

The displayed signals' magnitude was now 101.6% ±2.2% of the injected amount. The standard deviation of 2.2% taken into account, this was found to be satisfactory. A standard curve was made by injecting different amounts of mercury, and the result is shown in Table 7 and Figure 20.

Table 7: Points on a standard curve. Injected and measured amounts of mercury (conditions described in section4.2.2).

Injected(pg)	Measu.(pg)
173	176
86.5	88.1
43.2	42
17.3	15.3

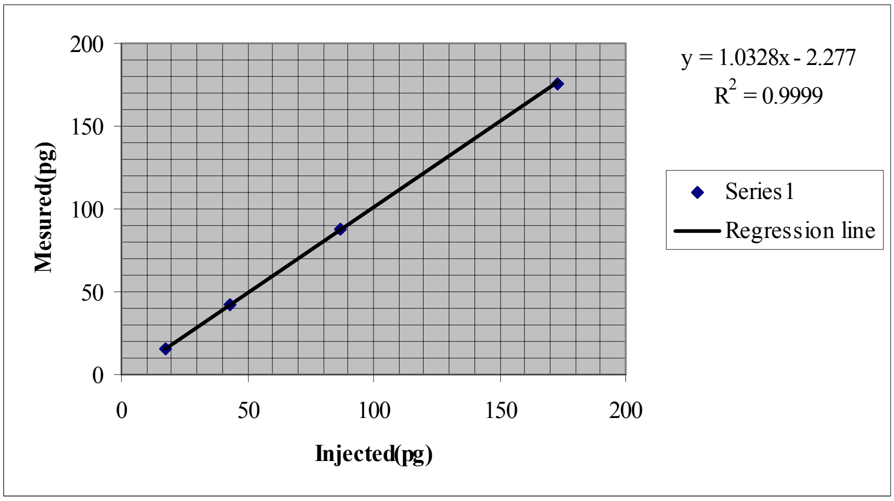

Figure 20: Standard curve made on the GARDIS monitor. Measured signals plotted against injected mercury amounts (conditions described in section 4.2.2).

A regression analysis showed a linear response over the area of interest.

Even though this initial calibration of the monitor showed good results, the GARDIS was not a very stable instrument to work with. Stability, background and response could change from day to day and it was therefore necessary to perform daily calibrations. These were made according to the procedure in section 4.1.5.

6.1.3 Checking the denuder coating

A binocular stereo microscope (WILD M3B, Heerburg, Switzerland), was used to take pictures of a coated denuder, in order to be able to view the structure of the coating. The pictures are presented in Figure 21 and Figure 22.

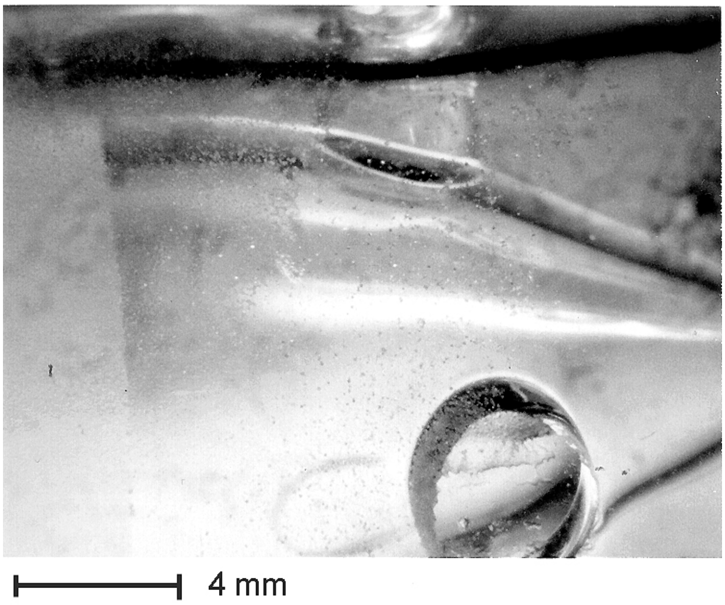

Figure 21: Microscopy picture of denuder. The picture shows the inlet end of the inner quarts tube in the denuder. The KCl salt coating is barely visible. The circular shapes on the figure relates to the points where inner and outer tube are connected.

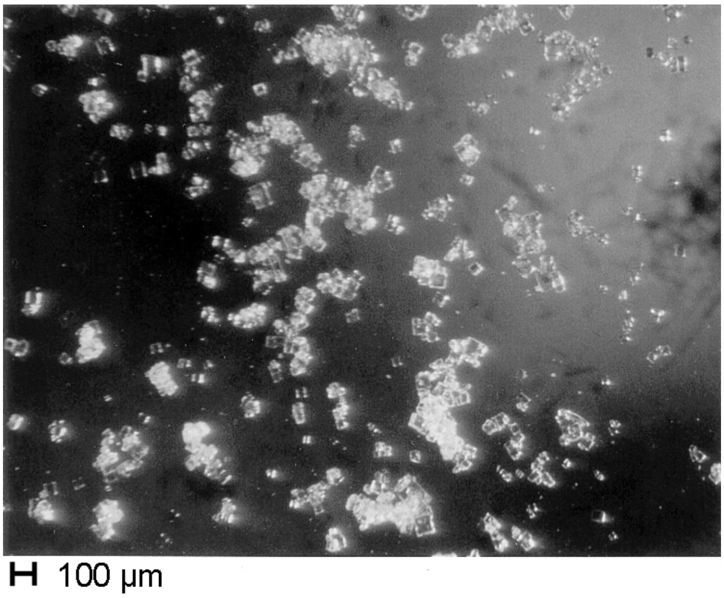

Figure 22: Microscopy picture of the denuder coating. Picture taken from outside of outer tube, directed against outside of inner tube.

The pictures were sent to Dr Xinbin Feng[49] for evaluation. He had previously studied microscopy pictures of the denuders used by Swedish researchers. He thought the salt coating appeared to be nice and evenly spread on the active surface, and that the layer seemed sufficiently "thick" to make the denuder collect all GDM in air passing through (good enough efficiency).

6.1.4 Introduction of the pyrolysis tube

Scientists at Swedish Environmental Research Institute and Chalmers University of Technology, informed that it was very important to connect a pyrolysis tube between the denuder and the GARDIS inlet. The purpose of the 900°C warm quarts tube was to combust any organic species interfering in the sample. The beads were put inside to increase the hot surface and thus the effect of the heat. Conditions are described in section 4.2.4. Four different injections were made and the results are described in Table 8.

Table 8: Calibration injections with pyrolysis tube connected. "Average" means the signal intensity relative to the injected amount of mercury (average recovery) (conditions described in section 4.2.4).

Connected	
Average(%)	59.9
St.dev(%)	6.3
Rel.st.dev	10.5 %
Count	4

Before the tube was connected, the signal intensity relative to injected amounts was about 100%. As Table 8 states, the signal intensity was decreased to only 59.9% ±6.3% after the connection of the tube. Since the quarts in the tube and the beads were new, and had not been cleaned in Br-Cl-solution before, it was thought that it could be in some way polluted. After thorough cleaning and rinsing the empty tube was connected in the system and new injections were performed. Results in Table 9.

Table 9: Calibration injections with rinsed and empty tube connected. "Average" means the signal intensity relative to injected mercury amounts (average recovery) (conditions described in section 4.2.4).

Empty	
Average	79.9
St.dev	4.2
Rel.st.dev	5.2 %
Count	5

The result of 79.9% ±4.2% signal intensity was better than prior to the cleaning, but still far from 100%. The beads were then filled into the tube, and the experiment repeated. Results in Table 10.

Table 10: Calibration injections with cleaned tube and beads connected. "Average" means the signal intensity relative to injected mercury amounts (average recovery) (conditions described in section 4.2.4).

Filled	
Average(%)	53.9
St.dev(%)	4.7
Rel.st.dev	8.7 %
Count	4

The signal intensity was too low, and the cleaning had apparently not been successful. At this point no apparent explanation was found. After consulting Ingvar Wangberg at Swedish Environmental Research Institute[51], the tube was disconnected during the field studies at Ny-Ålesund, Svalbard in the spring of 2000. He thought that the air in the arctic environment contained such small amounts of possible interfering organic components, that the pyrolysis tube would not be necessary.

Later, many similar experiments were carried out. The GARDIS monitor was very unstable, giving different results from experiment to experiment, and from day to day. This lead to the belief that the low signal intensities, might not be because of the pyrolysis tube, and every part of the system was tested and investigated. However, no conclusions could be made.

In the beginning of the field study on the Mediterranean Sea, the tube was connected. No mercury could then be detected on the sample denuders at all. Tests were performed in which one sample was analysed with the tube connected and another sample with the tube disconnected. As Table 27 in section 6.2.3 states, the mercury signal disappeared every time the tube was connected in the analysis system. The tube was therefore disconnected permanently.

Later on, discussions with Xinbin Feng[49], lead to a conclusion as to what might be the reason for all the problems with the pyrolysis tube. The GARDIS monitor chosen for this study, was originally built to measure outdoor air. Using zero air as a carrier gas when an introduction system was connected, was consequently a natural choice. The Swedish research groups all used a different analyser that required the use of argon as a carrier gas. Using argon, no oxygen was available for the combustion of organic components, and the pyrolysis tube had to be connected. On the other hand, in the system described here, where the carrier gas was zero air, a lot of excess oxygen was available and the pyrolysis tube thus not necessary. Conversely, the combination of excess oxygen and the high temperature could have led to the formation of HgO. Meaning that the mercury from the denuder sample would not have been collected on the gold traps, and consequently not detected. A quite plausible explanation taking into account the low signal intensity measured when the tube was connected.

6.1.5 The effect on precision when changing the sample introduction times

The precision of the GARDIS at varying introduction times was tested out by sampling and measuring mercury in the laboratory air. Conditions are described in section 4.2.5. The results are presented in Table 11 below.

Table 11: The impact on precision of changing sample introduction times. Volume is total volume of air entering the analyser before a measurement is made. Time is how many seconds the analyser was sampling before quantifying the mercury concentration. Average and standard deviation are given in ng/m3. Laboratory air was sampled (conditions described in section 4.2.5).

Time(s)	Volume(L)	Conc(ng/m3)			
300	0.5	8.798		Average	8.7
300	0.5	8.784		St.dev	0.1
300	0.5	8.556		Rel.st.dev.	1.6 %
240	0.4	7.896		Average	7.7
240	0.4	7.184		St.dev	0.4
240	0.4	7.952		Rel.st.dev.	5.6 %
180	0.3	7.66		Average	7.0
180	0.3	6.628		St.dev	0.5
180	0.3	6.859		Rel.st.dev.	7.7 %
120	0.2	7.201		Average	6.9
120	0.2	6.858		St.dev	0.2
120	0.2	6.775		Rel.st.dev.	3.3 %
60	0.1	8.228		Average	6.2
60	0.1	6.86		St.dev	2.5
60	0.1	3.43		Rel.st.dev.	40.0 %
30	0.05	8.229		Average	3.2
30	0.05	0.678		St.dev	4.4
30	0.05	0.571		Rel.st.dev.	139.0 %

The results show that the measurements became less precise when the shortest introduction/sampling times were used. The short introduction/sampling times were connected to very small volumes of air introduced in the detector for each measurement, meaning that also very low concentrations were measured. A reason why the precision was so poor in small samples, could be that small contaminations from the surroundings caused severe changes in the measured concentrations.

The measurements being the concentration of mercury in laboratory air, would change if the mercury amount in the laboratory changed. The experiments were, however, performed during the night, and very small variations in mercury concentrations were expected then.

6.1.6 Memory effects

To reveal any memory effects in the detection system when very short introduction times were used, one large injection of mercury was made and measured. The system was then allowed to run for a while, making consecutive measurements without more mercury being injected. See Table 12.

Table 12: Memory effect in the GARDIS after injecting saturated mercury air, using very short sample introduction times. "BG" is background measurements, meaning no mercury is injected, and just the signal from the system is measured. "CALIB" means injection of mercury to the system. "Time" is the sample introduction time (conditions described in section 4.2.6).

Measurement	Injected(pg)	Time(s)	Result(pg)
BG	0	60	1.9
BG	0	60	1.9
BG	0	60	1.8
CALIB	223.8	60	176.3
BG	0	60	97.9
BG	0	60	32.6
BG	0	60	18.8
BG	0	60	13.4
BG	0	60	10.4
BG	0	60	8.2
BG	0	60	7.1
BG	0	60	6
BG	0	60	5.1
BG	0	60	5
BG	0	60	4.1
BG	0	60	3.6

The experiments showed a significant memory effect. The same effect was, on the other hand, not observed at longer sample introduction times. Since GDM measurements requires a long introduction time due to the heating, the memory effect is hardly a problem there, but if the monitor was to be used to make TGM measurements in a very polluted environment, the problem could be serious. The test above was performed in connection with an assignment where TGM concentrations in a former paper mill were to be determined. Decades ago, mercury was used as a fungicide in paper production. It was suspected that high levels of mercury were still present at the premises where the fungicide was once used. The measured concentrations were to be compared against the permitted levels of mercury in a working environment. Since the allowed maximum mercury level was 50 000 pg/L, and the GARDIS could detect at the most 1000 pg, very small air volumes were required, and the memory effect problem would be substantial.

The sample introduction time and flow resulted in a total introduced volume of only 100 ml. A potential risk was that not all of the volume in the introduction system was exchanged during the introduction. Mercury could then be left in the system giving rise to signals in later measurements. Tubing and filter volume was lowered to a minimum to test the theory, several consecutive experiments were performed, and the memory effect disappeared completely.

It was clearly important to keep the total volume of the system in mind when measuring mercury in small volumes of air/gas.

6.1.7 Modifications on the denuder oven

Ideally the temperature in the denuder during desorption should be between 450°C and 500°C. Lower temperatures might not be sufficient to desorb all the mercury completely, and higher temperatures will degrade the coating more rapidly. Experiments performed by Swedish scientists[48] proved that after 10 min of heating at temperatures between 450°C and 500°C, no more mercury was released, so the denuder should be kept at the desorption temperature for as close to 10 minutes as possible. The temperatures measured in the denuder during the desorption cycle, before any modifications were done to the custom made denuder oven, are plotted in Figure 23. Conditions are described in section 4.2.7.

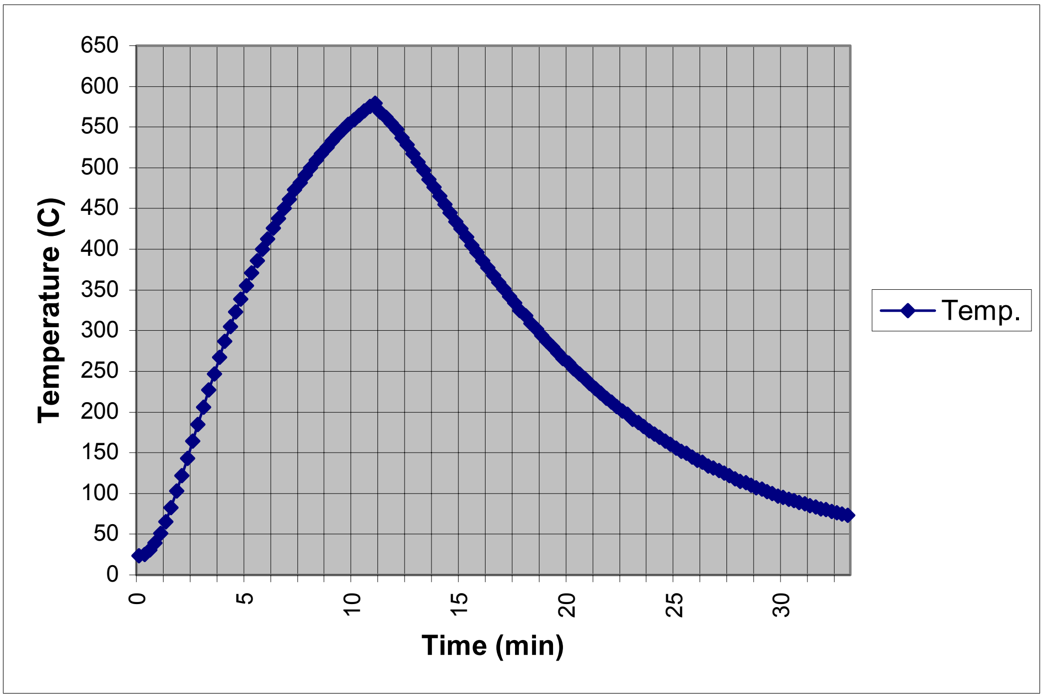

Figure 23: The temperature variations in the denuder during desorption. Denuder oven version one. Temperature in denuder plotted as a function of time in the heating cycle (conditions described in section 4.2.7).

As the figure shows, the denuder needed about 8 min to reach the desired temperature of at least 450°C. In order to prevent the temperature from falling below 450°C immediately, an "overshoot" up to nearly 600°C had to be tolerated. Nevertheless the desorption window (temperature > 450°C), was only about 7 min long. The cooling time from 450°C to 100°C (when the denuder can be taken out of the system), was about 15 min. If the oven was used for several consecutive desorptions, the initial temperature increased, and so did the overshoot. After completing the modifications described in section 4.2.7, the temperatures in the denuder during desorption were measured again and the results plotted in Figure 24.

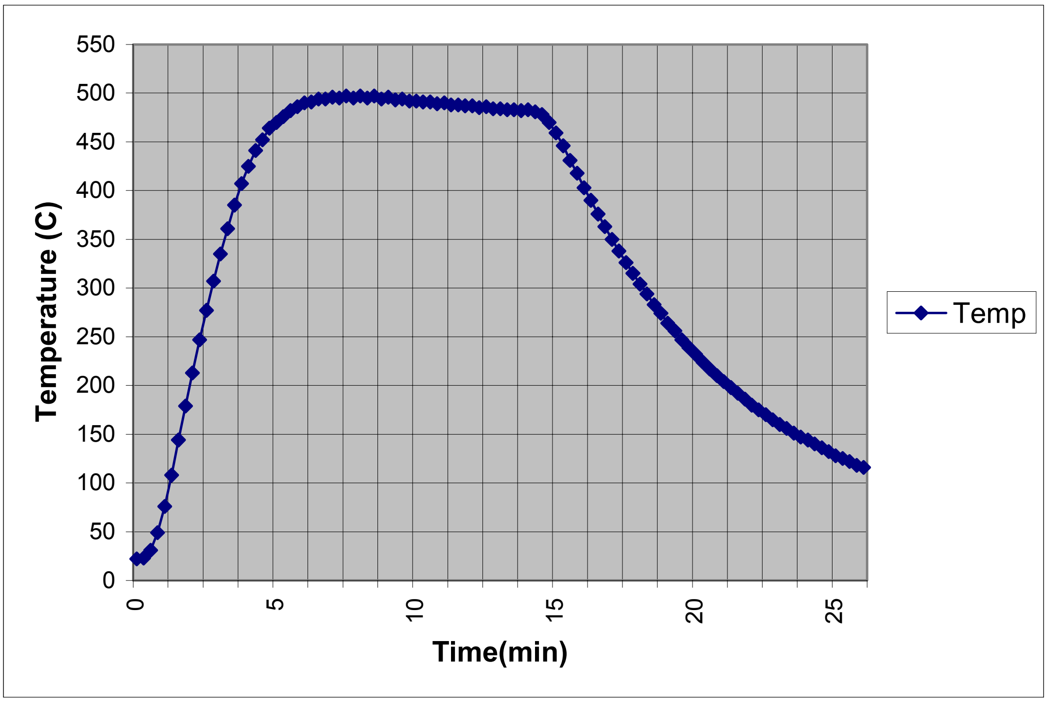

Figure 24: The temperature variations in the denuder during desorption. Modified denuder oven. Temperature in denuder plotted as a function of time in the heating cycle (conditions described in section 4.2.7).

Time and cost did not allow a complete redesign, so the modifications were limited by the original enclosure. The modifications did nevertheless give significant changes in the temperature curve were. The heating time was reduced to 5 min. The temperature was kept stable at about 500°C for ca 10 min, and then the denuder was cooled down to 100°C in less than 10 min.

The procedure time for the desorption of denuders had been reduced from 30 min to 25 min, while the temperature window had increased from 7 min to the desired 10 min. In addition, the desorption temperature was stable, controllable and with no damaging overshoot.

The installation of a delay circuit (see section 4.2.7) to prevent the fuses from blowing when the oven was turned on, made the previous voltage stabiliser redundant. The stabiliser weighed about 17 kg, and the system became far more mobile after removing it.

6.1.8 The influence of introduction time on signal magnitude

The opportunity to carry out the daily calibrations using much shorter sample introduction times than during sample analyses, would save the operator much time each day. According to the manufacturer of the GARDIS, the sample introduction time should not affect the magnitude of the signal, provided that the correct system background value was subtracted from all signals.

Two calibration series were performed as described in section 4.2.8. The first had introduction times of 900 s, same as the samples, and the other 120 s. The two curves are plotted in Figure 25 below.

It was evident that the signal magnitude was dependent on the sample introduction time, and that the GARDIS had to be calibrated using the same introduction times as during sample analysis. Further investigations should be carried out to find an explanation to the phenomenon.

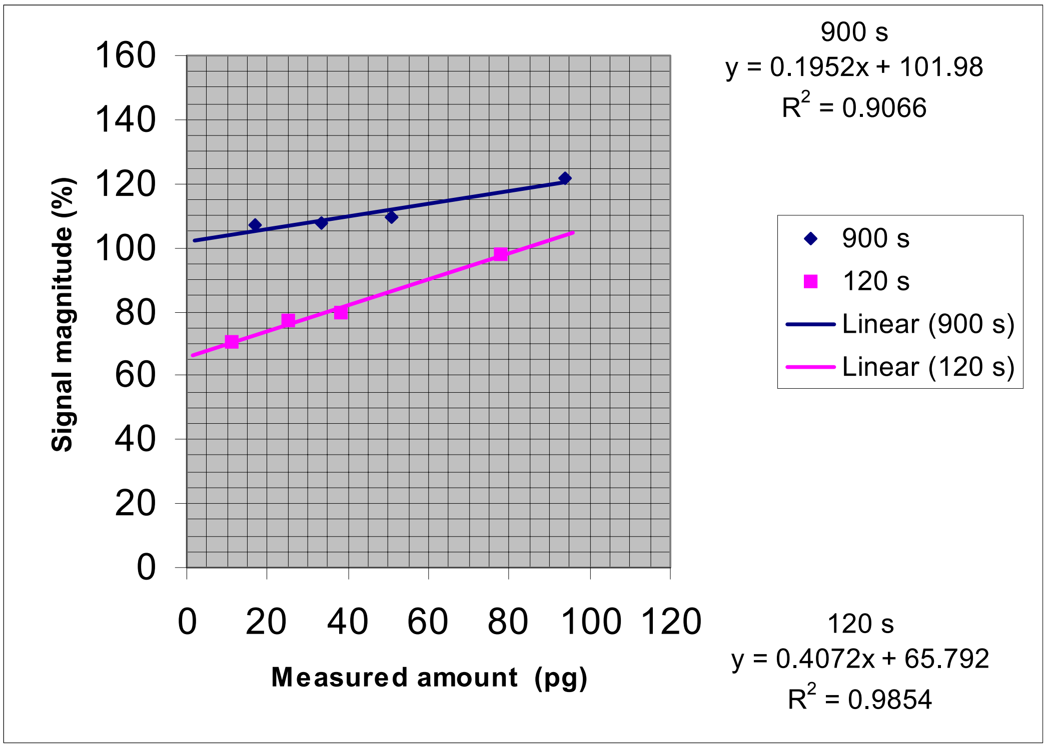

Figure 25: Standard curves for introduction times of 900 and 120 seconds. The signal intensity relative to injected mercury amount is plotted against the measured signal (conditions described in section 4.2.8).

6.1.9 Introduction of the soda lime trap

The process of cleaning the denuders, as described in section 4.1.4, was very time consuming and the denuders did not seem to become properly clean. The procedure became even more time consuming after the removal of the pyrolysis tube. Since Hg is supposed to be desorbed from the denuder in about 10 min at the desorption temperature (450-500°C), a different contaminant was suspected to be constantly released from the denuder, giving rise to a signal in the detector. Mary Lynam[52] at The University of Michigan, recommended to try out a soda lime trap (quarts tube filled with soda lime pellets). The US-group had suspected a co-adsorbent coating the gold traps during measurements in rural areas, and the soda lime trap was put in front of the analyser to overcome the problem. A soda lime trap was then put into the system in the same position as the pyrolysis tube used to be. Before the trap was used in "real" GDM measurements, a test was performed to see if the trap adsorbed any Hg. A standard curve was made (see section 4.2.9), first without the trap connected, and then with the trap, and the two curves were compared in Figure 26 below.

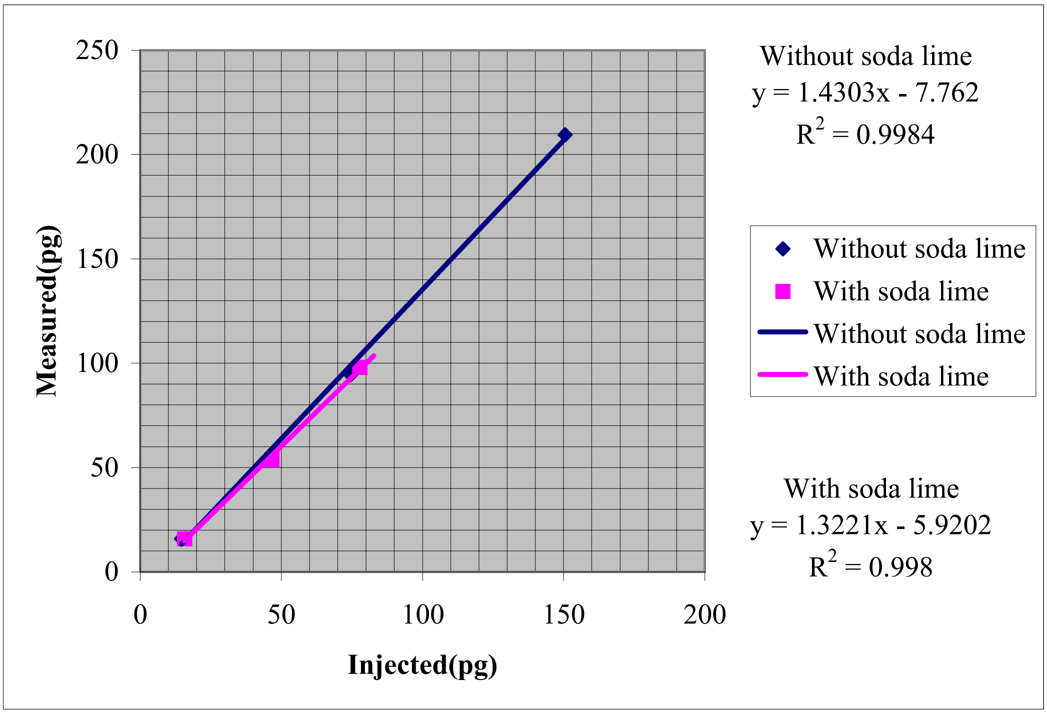

Figure 26: Comparison of standard curves made without and with, the soda lime trap connected in the system. Measured amount of mercury is plotted against injected amount (conditions described in section 4.2.9).

There was hardly any difference between the two curves, and it was concluded that the trap did not remove any of the Hg in the passing air.

Two denuders were then thermally cleaned. The first denuder was cleaned without the soda lime trap connected (see Table 13), and in the second case the trap was connected (see Table 14).

Table 13: Cleaning series of denuder without the soda lime trap connected. "BG" means background measurement, no denuder is desorbed (conditions described in section 4.2.9).

Type	Time(s)	Measur.(pg)
BG	900	5.6
den2	900	93.9
den2	900	22.2
den2	900	19.8
BG	900	8.8
BG	900	7.7
den2	900	10.6
den2	900	13.6
BG	900	9.5
BG	900	7.7

As the table shows, the cleaning procedure could take as long as 3-4 hours including the cooling between desorptions, without the soda lime trap connected.

Table 14: Cleaning series of denuder with the soda lime trap connected. "BG" means background measurement, no denuder is desorbed (conditions described in section 4.2.9).

Type	Time(s)	Measur.(pg)
BG	900	3.9
den8	900	13.1
den8	900	5
BG	900	2.9

After connecting the trap, the same process took approximately one hour, and the denuders gave virtually no mercury signal when tested.

The time spent on each denuder for analysis and cleaning was thereby reduced by 2-3 hours.

In addition, the measured values of mercury concentration in the laboratory air were reduced from an extremely high level, to the expected concentration when the trap was connected. These results are described in section 6.1.10.

Soda lime is known to remove free halogens that might deactivate the gold trap, and thus reduce the mercury signals. The opposite did, however, seem to be the problem in this case. Elevated levels of mercury were measured. Soda lime was previously used as a sampling device for CO_2 in air. However, CO_2 will normally not absorb radiation in the Hg area (around 250 nm). An effort should be made to map the potential interfering species removed by the soda lime trap. See also section 2.5.

6.1.10 Breakthrough tests

The conditions during the following experiments are described in section 4.2.10. The efficiency of the denuder as a GDM sampler, was tested out by coupling two denuders in series, sample laboratory air, and quantify the mercury amount on both denuders to see how much the first denuder failed to collect. Until this test was performed, all samples had been collected using a sampling time of about 24 hours, and sampling flows between 3 and 4 L/min. Four breakthrough tests were performed with varying sampling flows. See Table 15.

Table 15: Breakthrough tests using different sampling flows. Sampling time was about 24 hours for all tests. "Pos." indicates the position of the denuder during sampling (front or back). Total amount of mercury on both front and back denuder was used to calculate the concentration in the laboratory air. "Distr." shows the relative amount of mercury on front and back denuder. No pyrolysis tube or soda lime trap was connected (conditions described in section 4.2.10).

Date	Flow (l/min)	Volume (m3)	Den	Pos	Measu. (pg)	Total (pg)	Conc (pg/m3)	Distr (%)
2001.03.23	2.77	3.9595	3	F	181.3			47.7
2001.03.23	2.77	3.9595	2	B	199	380.3	96	52.3
2001.03.24	3.55	4.3997	13	F	194.4			45.8
2001.03.24	3.55	4.3997	12	B	230.1	424.5	96.5	54.2
2001.03.26	3.54	4.47519	13	F	187.9			41.5
2001.03.26	3.54	4.47519	11	B	264.6	452.5	101.1	58.5
2001.03.27	0.36	0.33188	13	F	201.7			73.4
2001.03.27	0.36	0.33188	12	B	73.1	274.8	828	26.6

Ideally all the mercury should be collected on the front denuder. This was obviously not the case, even when the flow was reduced significantly. A major breakthrough of 26-58% was observed at all sampling flows. The calculated concentrations in the laboratory air were also substantially higher than expected. The soda lime trap was connected in the analysis system as another test was performed. See Table 16.

Table 16: Breakthrough test. Conditions and table identical to Table 15. Soda lime trap connected during analysis (conditions described in section 4.2.10).

Date	Flow (l/min)	Volume (m3)	Den	Pos	Measu. (pg)	Total (pg)	Conc (pg/m3)	Distr (%)
2001.03.30	2.41	3.45449	8	F	8.5			44
2001.03.30	2.41	3.45449	12	B	10.8	19.3	5.6	66

The concentration of mercury in the laboratory was calculated to be 5.6 pg/m^3, a much more probable concentration than earlier calculated. This might have been due to the soda lime trap removing an interfering specie that increased the signal radically. The extent of the breakthrough was, however, still significant. It was decided to put a new and, if possible, thicker coating on one of the denuders, and a new test was performed. See Table 17.

Table 17: Breakthrough test. Conditions and sampling time same as tests in table 15. New coating on denuder 9 (conditions described in section 4.2.10).

Date	Flow (l/min)	Volume (m3)	Den	Pos	Measu. (pg)	Total (pg)	Conc (pg/m3)	Distr (%)
2001.04.02	3.52	4.54196	9	F	14			62.2
2001.04.02	3.52	4.54196	5	B	8.5	22.5	5	37.8

The result was somewhat improved, but was still not considered satisfactory. Two new tests were then executed, were the flow was substantially increased. See Table 18.

Table 18: Breakthrough tests. Increased flow. New coating on denuder 9. Same conditions as in table 15 (conditions described in section 4.2.10).

Date	Flow (l/min)	Volume (m3)	Den	Pos	Measu. (pg)	Total (pg)	Conc (pg/m3)	Distr (%)
2001.04.04	6.26	7.13983	9	F	15.1			72.2
2001.04.04	6.26	7.13983	13	B	5.8	20.9	2.9	27.8
2001.04.04	5.9	6.729	3	F	13.3			63.9
2001.04.04	5.9	6.729	5	B	7.5	20.8	3.1	36.1

Seemingly, the combination of new coating and higher sampling flow improved the result further. Consulting research groups working on GDM measurements in Canada and USA, revealed the possibility of Hg "wandering" in the system. Recent tests had shown that the Hg might drift out of the denuder if the sampling took a long time. A sampling time of no longer than 6 hours was therefore recommended. Two new tests were performed, using sampling times of about 5.5 hours. Results are in Table 19.

Table 19: Breakthrough tests. Sampling time about 5.5 hours. New coating on denuder 9. Conditions as in table 15 (conditions described in section 4.2.10).

Date	Flow (l/min)	Volume (m3)	Den	Pos	Measu. (pg)	Total (pg)	Conc (pg/m3)	Distr (%)
2001.04.05	5.89	1.97349	9	F	7.2			100
2001.04.05	5.89	1.97349	13	B	-0.8	7.2	3.65	0
2001.04.05	6.16	2.06289	3	F	5			65
2001.04.05	6.16	2.06289	5	B	2.7	7.7	3.73	35

Short sampling time, high flow and a thicker coating seemed to give very good results. The coating procedure was then set to be as described in section 4.1.2, to make the coating as thick as possible. All denuders were recoated.

6.1.11 The limit of detection

The limit of detection for the introduction and analytical system was found by performing the experiment described in 4.2.11. Ten consecutive background measurements were made and the results are presented in Table 20.

Table 20: Background measurements in introduction and analytical system. Limit of detection calculated (conditions described in section 4.2.11).

Type	Value
Count	10
Average(pg)	2.1
Minimum(pg)	1.9
Maximum(pg)	2.5
St.deviation(pg)	0.2
LOD	0.6

The limit of detection was defined as 3 times the standard deviation of the measurements, and calculated consistent with that. The GARDIS monitor is, according to the manufacturer, supposed to have a detection limit of 0.5 pg. The calculated limit of detection of 0.6 pg for the whole introduction system and the GARDIS, was therefore considered satisfying.

The experiment for deciding the limit of detection for the whole sampling and analysis procedure, is described in section 4.2.11. Five blank denuders were analysed after being treated just like ordinary samples. See Table 21.

Table 21: Measurements of blank samples. Limit of detection calculated (conditions described in section 4.2.11).

Type	Value
Count	5
Average(pg)	-0.1
Minimum(pg)	-1.3
Maximum(pg)	0.5
St.deviation(pg)	0.7
LOD	2.1

The limit of detection was defined as three times the standard deviation of the measured blank samples, and was calculated to be 2.1 pg. The obtained LOD of 2.1 pg, combined with the optimised sampling conditions (flow 6 L/min, sampling time about 6 hours), corresponds to a detection limit of about 1 pg/m^3.

The same experiment was performed on the Zeppelin Mountain during the field study in the spring of 2001. Limits of detection were calculated in the same way as above. Sampling and analysis conditions are described in section 5.1.2, and results are given in Table 22 and Table 23.

Table 22: Background measurements in introduction and analytical system at Svalbard spring 2001. Limit of detection calculated (conditions described in section 5.1.2).

Type	Value
Count	10
Average(pg)	1
Minimum(pg)	0.6
Maximum(pg)	1.7
St.deviation(pg)	0.4
LOD(pg)	1.2

Table 23: Measurements of blank samples at Svalbard 2001. Limit of detection calculated (conditions described in section 5.1.2).

Type	Value
Count	10
Average(pg)	-0.5
Minimum(pg)	-4.1
Maximum(pg)	6.4
St.deviation(pg)	2.8
LOD(pg)	8.4

Evidently the limits of detection, both for introduction and analytical system and for the whole process, were significantly increased. The 8.4 pg LOD corresponds to a limit > 4 pg/m^3. Since the experiments had been performed as before, it appeared that the working conditions in the field led to higher detection limits. Ideally, it should be possible to obtain the same detection limits working in the field, as in the laboratory, but several parameters could have contributed to the enlarged limits of detection. All of the equipment, including the GARDIS, had been transported a long way, and there was no time to stabilise the system for several weeks as was possible before doing the experiments in the laboratory at NILU. The air in the “laboratory room” at the Zeppelin Mountain might not have been as clean as in the laboratory at NILU, and the denuders had to be handled outside, sometimes in snow, rain and wind. A possibility could also have been more unstable electricity than on the main land. The GARDIS signal would be highly affected by electricity changes.

At the Zeppelin Mountain, a Tekran Model 2537A-Mercury Vapour Analyser was constantly measuring TGM in ambient air (online system). To see if any improvements concerning limits of detection could have been achieved using another analyser, the Tekran was connected to the GDM introduction system, and a series of background measurements were made. Conditions were identical to those in section 5.1.2, except from the GARDIS being exchanged for the Tekran. Results are presented in Table 24.

Table 24: Background measurements for introduction and analytical system using Tekran for analysis. Svalbard spring 2001. Limit of detection calculated (conditions described in section 5.1.2).

Type	Value
Count	10
Average(pg)	0.74
Minimum(pg)	0.46
Maximum(pg)	0.9
St.deviation(pg)	0.14
LOD(pg)	0.42

The limit of detection, concerning introduction and analysis system, using the GARDIS was 1.2 pg. Exchanging the GARDIS for the Tekran, led to a decrease in the limit to 0.42 pg. This was almost one third of the GARDIS limit, and the benefit from using a Tekran monitor to quantify the samples would probably be considerable. The manufacturer of the Tekran unit states the detection limit to be 0.2 pg. By optimising the conditions in the field, the limit might therefore be further improved.

6.2 Field studies

6.2.1 Ny-Ålesund, Svalbard spring 2000

On February the 10th 2000, a group of US scientists reported the first observations of elevated GDM concentrations during TGM depletion episodes at Barrow[53]. Measurements at Svalbard were performed in April and May 2000, according to accounts in section 5.1.1. The results are presented in Table 25 below, and are visualised in Figure 27.

Table 25: Results of GDM and TGM measurements at Svalbard, 2000. The table states date, pump number used during sampling, total sample volume, number of sample denuder, measured amount of GDM, calculated concentration of GDM in ambient air, average concentration if two samples were analysed and TGM concentrations (conditions described in section 5.1.1).

Date	Pump	Corr.Vol (m3)	Denuder	GDM (pg)	GDM. (pg/m3)	Average (pg/m3)	TGM (ng/m3)
2000.04.29	5	4.819	3	1.2	0.25		
2000.04.29	1	4.609	4	20.7	4.49	2.4	1.3
2000.04.30	5	4.989	3	11.2	2.25		
2000.04.30	1	4.846	4	4.5	0.93	1.6	1.4
2000.05.03	1	5.803	3	34.2	5.89	5.9	0.7
2000.05.04	5	5.163	1	34.9	6.76		
2000.05.04	1	4.948	3	26.5	5.36	6.1	0.6
2000.05.05	5	4.923	2	59.9	12.17	12.2	0.3
2000.05.06	5	5.9	3	56.4	9.56	9.6	0.6
2000.05.07	1	4.214	2	12.2	2.88	2.9	1.2
2000.05.10	1	5.839	2	28.9	4.94	7.8	0.2
2000.05.14	5	4.026	2	40.5	10.06	8.2	0.5

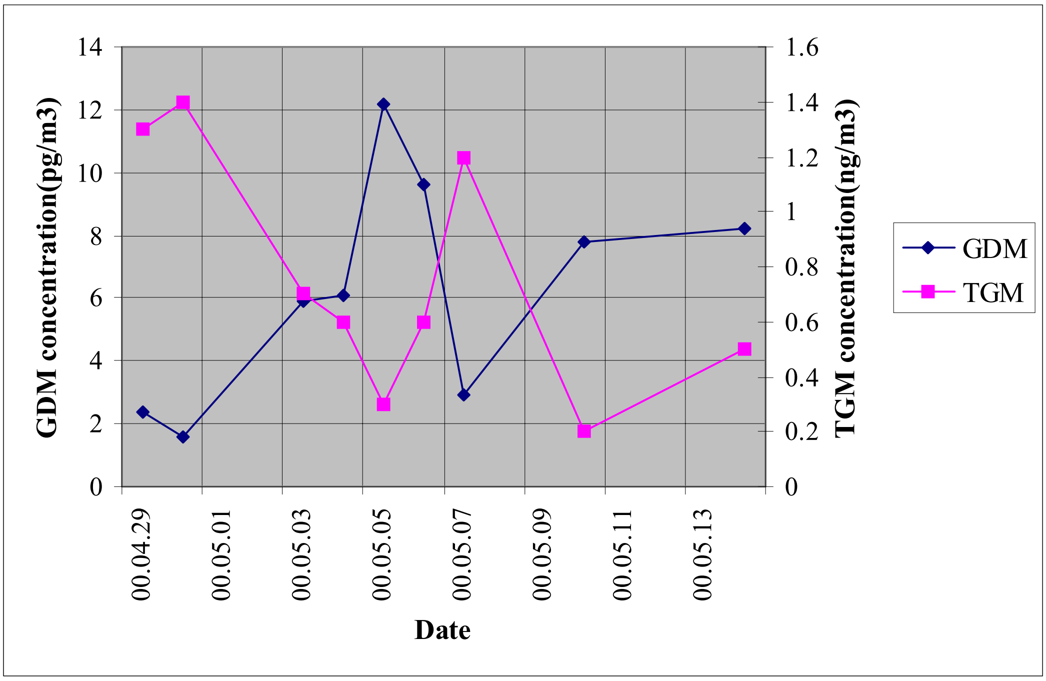

Figure 27: GDM and TGM concentrations. Daily variations, spring 2000 (conditions described in section 5.1.1).

As the measurements were performed at an early stage in the method development, numerous problems occurred. No modifications had yet been performed on the denuder oven, and this made both analysis and denuder cleaning very time consuming. Neither pyrolysis tube, nor soda lime trap was connected. In addition to the denuder cleaning process being time consuming, the denuders did not seem to be properly cleaned. This might have been caused by an interfering specie, as explained in (soda lime trap section 6.1.9). The result of all the time consuming procedures and problems was that there were not enough time to calibrate the system properly, to analyse two parallel samples or to analyse blank denuders. On the 29th and 30th of April, where two parallel samples were analysed, the parallels deviated substantially from each other (see Table 25). The quality of the data obtained may therefore be questioned. On the 4th of May, however, the parallels were quite similar.

The placing of the sampling box, 1.5 m above a metal grating floor, was not ideal. Most metal items contain small amounts of mercury. If mercury was released from the grating, the samples could be contaminated, leading to a positive bias on the results. Given the cold climate at the Zeppelin Mountain (temperature mostly below 0°C), the probability of mercury vaporising from the floor to a substantial degree, was minor.

Despite the uncertainty connected to the measurements, the results in Table 25 and Figure 27 show a surprisingly good agreement with the theory being tested out (section 1.6.2.2.). The GDM concentrations seemed to rise as soon as the TGM values dropped.

The GDM and TGM concentrations seemed to be highly dependent, and the negative correlation is plotted in the figure below. Taking into account the quality of the data, a correlation coefficient of 0.8 is very satisfying. The theory of the Arctic depletion episodes suggests that GDM is formed when TGM is oxidised in the air. The measured concentrations relates very well to this theory. Additional data, and more reliable data, must however be obtained before any conclusions can be drawn.

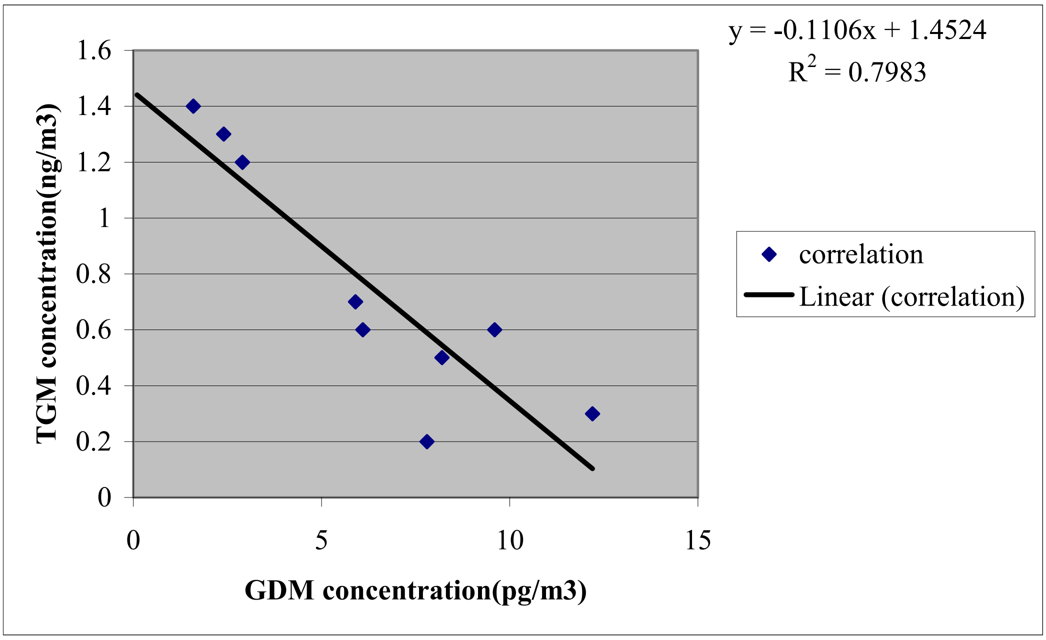

Figure 28: The negative correlation between GDM and TGM concentrations measured at Svalbard spring 2000 (conditions described in section 5.1.1).

6.2.2 Ny-Ålesund, Svalbard spring 2001

To obtain further data on the variation of GDM and TGM concentrations in the Arctic, an additional sampling campaign was performed in the spring of 2001. Compared to the campaign of spring 2000, several parameters had been optimised. All sampling and analysis conditions are described in section 5.1.2. The measured GDM and TGM concentrations are presented in Table 26 and visualised in Figure 29.

The atmospheric activity for mercury was not as high in spring 2001 as it was spring 2000. Only one TGM depletion episode was observed, on the 21st of April. The GDM concentration did, however, rise significantly on this date. On the 15th of April a very high concentration of GDM was measured as well, albeit the TGM concentration being stable (not decreased). One possible explanation to the increased GDM amount could be that the wind force was close to storm on this day. The heavy wind could have effected or polluted the sampling denuders. It can also be noted that a possible dependence between GDM concentration and wind force was observed in the measurements from the Mediterranean Sea (see section 6.2.3).

Table 26: Results of GDM and TGM measurements at Svalbard 2001. The table states date, pump number used during sampling, sampled air volume, time of sampling, sampling flow, denuder number, measured GDM amount, calculated GDM concentrations, average GDM concentration between sample parallels, averaged TGM concentration over the same period of time and standard deviation for the TGM measurements (conditions described in section 5.1.2).

Date	Pump	Vol (m3)	T (min)	Flow (l/min)	Den	GDM (pg)	GDM (pg/m3)	Aver (pg/m3)	TGM (ng/m3)	st.dev (ng/m3)
01.04.13	1	1.75678	287	6.12	9	-3.4	0	0.9	1.62	0.17
	5	1.68476	287	5.87	11	3	1.78			
			300		2blind	-4.1				
01.04.14	1	2.00078	329	6.08	2	1.1	0.55	0.4	1.59	0.13
	5	1.93335	329	5.88	11	0.3	0.16			
			335		9blind	-2.7				
01.04.15	1	1.97393	330	5.98	2	45.8	23.2	24.7	1.6	0.12
	5	1.9198	330	5.82	9	50.2	26.15			
			345		11blind	-0.3				
01.04.17	1	2.06744	342	6.05	9	5.6	2.71	3	1.27	0.24
	5	2.0075	342	5.87	2	6.6	3.3			
			355		11blind	-1.4				
01.04.18	1	2.0814	343	6.07	9	6.6	3.17	2.5	1.79	0.07
	5	2.02612	343	5.91	11	3.8	1.88			
			345		2blind	-0.3				
01.04.19	1	1.99651	321	6.22	2	2.1	1.02	2.3	1.49	0.19
	5	1.8777	321	5.85	11	2.3	1.23			
			340		9blind	0.6				
01.04.20	1	2.12694	328	6.48	9	2	0.94	1	1.61	0.06
	5	1.90704	328	5.81	2	2	1.05			
			345		11blind	-1.8				
01.04.21	1	2.21957	342	6.49	9	29.6	13.34	13.3	0.88	0.39
	①5	¤	¤	¤	¤	¤	¤			
			365		2blind	6.4				
01.04.22	1	2.07287	337	6.15	2	7.1	3.43	3.6	0.91	0.28
	5	1.95751	337	5.81	8	7.5	3.83			
			340		9blind	-1.2				
01.04.23	1	2.00649	320	6.27	8	7.6	3.77	3.9	1.04	0.32
	5	1.8739	320	5.86	9	7.4	3.95			
			315		2blind	-0.1				
01.01.24	1	1.92393	310	6.21	9	3.8	1.98	2.9	1.15	0.31
	5	1.81641	310	5.86	2	6.9	3.81			
			305		8blind	②91.2				
01.04.25	1	1.9305	315	6.13	9	1.2	0.62	0.7	1.29	0.21
	5	1.8377	315	5.83	8	1.5	0.82			
			300		2blind	1.2				
01.04.26	1	2.2689	375	6.05	9	2.1	0.93	1.1	1.56	0.09
	5	2.15699	375	5.75	2	2.6	1.21			
			365		8blind	-2.8				

① The denuder could not be properly cleaned before sampling. Analysis showed a large negative signal. The denuder was exchanged for another denuder.

② Extremely large signal from the sample blank. Treated as an outlier and not used in calculations.

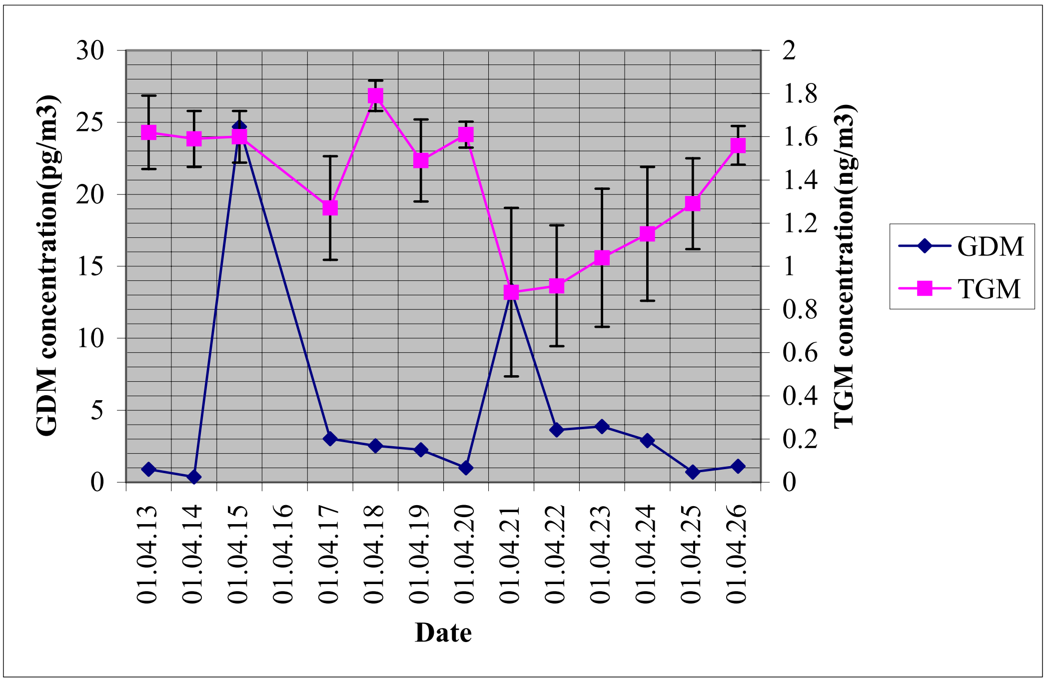

Figure 29: GDM and TGM concentrations 2001. Midday results (conditions described in section 5.1.2).

Since most of the blank values varied around zero, and many of them were negative, it was decided not to subtract them from the sample results. Subtracting the blank values obtained from day to day could just as likely add to the error in the measurements, as reduce them. Optimising sampling and analysis conditions, as well as procedures, might stabilise the blank values, and thus also lower the limit of detection.

Considering the LOD of 8.4 pg obtained in the field (see Table 23, section 6.1.11), all of the measurement results were below the limit, except from the results obtained on the 15th of April. If the “laboratory” limit of 2.1 pg (see Table 21, section 6.1.11) could be attained also in the field, and even be lowered by using the Tekran monitor for quantifications, most of the results would be above the LOD.

Optimisations made since the field study of spring 2000 (described in the previous section), resulted in a more controllable method. Reducing the time consume gave the opportunity to calibrate the analytical system on a daily basis, as well as cleaning the denuders properly prior to use. As can be seen in Table 26, most of the daily parallels now correlated very well. Further optimisations might improve the results even more.

As described in section 5.1.2, the temperature in the sampling box was probably substantially lower than the desired 40°C during sampling. This might have resulted in some of the coating dissolving in condensation, although no humidity was visible in the denuders. There is now also an ongoing discussion among scientists on whether the sampling temperature might have a greater influence on sampling efficiency than earlier assumed.

The strong dependence between GDM and TGM concentrations observed in 2000, could not be seen in 2001. Much because of the high measured amount of GDM on the 15th of April. The only depletion episode observed, on the 21st of April, did nevertheless contribute to strengthen the TGM depletion theory.

6.2.3 The Mediterranean research cruise

The Mediterranean Oceanographic Cruise took place in late July and beginning of August 2000. Measurements and analysis were performed according to the descriptions in section 5.2. In addition to mercury measurements, parameters like wind force, humidity and temperature was recorded onboard the ship. Measured GDM concentrations and wind forces are presented in Table 27.

Table 27: Results of GDM and wind force measurements at the Mediterranean Sea summer 2000. The table states date, pyrolysis tube connceted (yes or no), pump number, denuder number, measured GDM amount, calculated GDM concentrations, average GDM concentration between sample parallels and averaged wind force over the same period of time (conditions described in section 5.2).

Date	Pyro.	Pump	Volume (m3)	Denuder	GDM (pg)	Conc. (pg/m3)	Average (pg/m3)	Wind (m/s)
2000.07.29	Y	1	4.246	2	0	0		
2000.07.29	Y	5	3.994	3	0	0	0	
2000.07.30	Y	1	3.57	8	0	0		
2000.07.30	Y	5	2.089	13	0	0	0	
2000.07.31	Y	1	3.257	10	0	0		
2001.07.31	Y	5	3.159	11	0	0	0	
2000.08.01	N	1	4.664	8	35.4	7.6	8.2	3.8
2000.08.01	N	5	3.471	9	30.2	8.7		
2000.08.02	Y	5	4.809	10	0	0		
2000.08.02	N	1	5.286	11	45.5	8.6	8.6	5.5
2000.08.03	Y(New)	5	3.735	9	0	0		
2000.08.03	N	1	5.023	8	78.3	15.6	15.6	5.4
2000.08.04	N	1	1.74	10	45	25.9		
2000.08.04	N	5	1.199	11	38.7	32.3	29.1	9
2000.08.05	N	1	4.582	8	56.5	12.3	12.3	7.8
2000.08.05	N	①5	2.335	9	44.4	19		
2000.08.06	N	1	4.245	11	36	8.5	8.5	4.5
2000.08.06	N	①5	1.604	13	27.1	16.9		

① Pump number 5 had been soaked in water, and was not working properly. These results were disregarded later.

The first days of the cruise, the sample denuders gave no mercury signal at all. It was suspected that the pyrolysis tube could affect the result. Analysis were then performed with and without the pyrolysis tube connected (one parallel with and one without). It appeared that whenever the pyrolysis tube was connected, no signal would show when samples were analysed. The tube was then disconnected for the rest of the cruise. For further explanations see section 6.1.4.

The expected GDM concentrations in the area were between 10 and 100 pg/m^3[54], and the measured values were clearly in the area. As described in section 5.2, the working conditions were not ideal onboard. The analysis system was highly unstable, and a reliable calibration virtually impossible to perform. As mentioned, it was suspected that the electricity was not stable. After returning from the cruise, the service files on the GARDIS monitor were sent to the manufacturer in Lithuania. After studying the files it was reported that unstable electricity was a plausible reason for some of the problems. The base line during the measurements had moved significantly several times a day, making the calibration highly unreliable.

The obtained results were compared to variations in temperature, humidity and wind force. No dependence could be observed between GDM concentrations and temperature or humidity, but the variations in GDM concentration seemed to follow the changes in wind force rather well. These variations and changes are visualised in Figure 30. Figure 31 shows the correlation between GDM concentration and wind force.

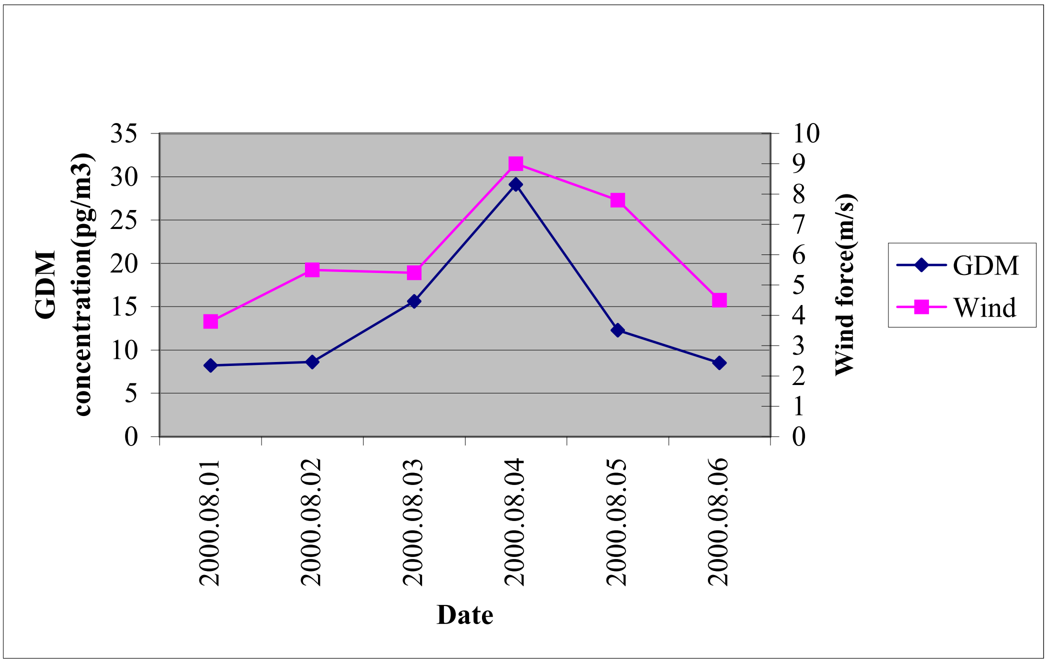

Figure 30: GDM concentrations and wind forces measured in the Mediterranean Sea summer 2000 (conditions described in section 5.2).

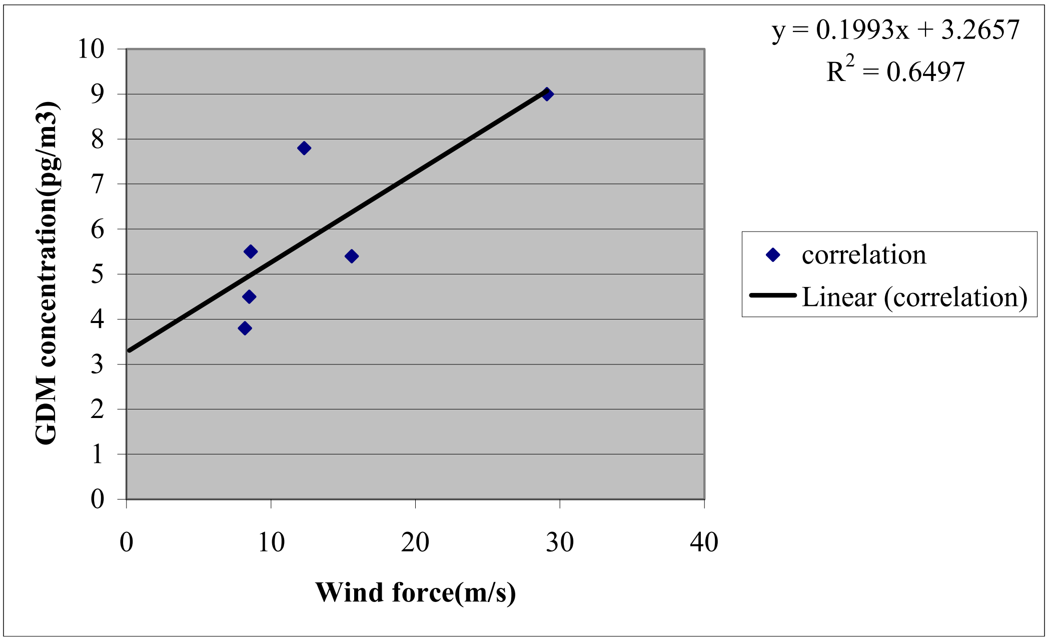

Figure 31: A plot showing the correlation between GDM concentration and wind force. Measurements made on the Mediterranean Sea 2000 (conditions described in section 5.2).

The variations seem to follow each other reasonably well, although a correlation coefficient of 0.65 is not a very strong indication. Far more data would have had to be collected in order to establish a confident dependence.

During the cruise, two other research groups measured GDM. An Italian group made 24 hour and 12-hour measurements using tubular KCl coated denuders. A Swedish group employed an automatic system with annular KCl coated denuders.

The Italian group did not obtain any 24-hour data during the period in Table 27, and reported 12-hour measurement results only from some of the dates. The Swedish system made several short time measurements a day. The results in Table 27 could therefore not be compared to the other results on a day-by-day basis.

The mean GDM levels measured in the period were however calculated for each group. The Italian group measured an average of 5.01 pg/m^3 and the Swedish group an average of 11.67 pg/m^3. The results in Table 27 averaged to 13.71 pg/m^3 and were thus quite similar to the results obtained with the automatic system using annular denuders.

7 Conclusions and recommendations

In order to sample gaseous divalent mercury (GDM) from ambient air, and quantify the concentrations, two systems have been built. A sampling system to collect the GDM from air, and a system to introduce the sample directly into a GARDIS - AAS mercury analyser.

The sampling system seems to work reasonably well concerning the sampling of GDM from ambient air. A better isolated sampling box will however be needed in order to control the sampling temperature.

The introduction system has undergone significant modifications throughout the study. The changes made to the denuder oven, together with the introduction of the soda lime trap, contributed to make the method less time consuming, more reliable, controllable and stable.

The GARDIS mercury analyser used for quantifications, has been very unstable. Considerable amounts of time have been spent, trying to calibrate and stabilise the unit. A test performed where the GARDIS was exchanged with a Tekran AFS mercury analyser, showed that the sensitivity of the analysis benefited significantly from the switch. The Tekran unit also showed a much higher degree of stability, and less extensive calibration procedures were necessary. Using the Tekran instead of the GARDIS in further studies, would probably decrease the time consume and increase the reliability of the measurements considerably.

The theory of GDM formation during depletion of elemental mercury in the Arctic, has been strengthened by the GDM sampling campaigns executed. The concentration of GDM seemed to increase as soon as the elemental mercury concentration decreased. To draw any conclusions, more data would however be needed. Preferably over longer periods of time, and with a system that has undergone far more validation tests. Future field studies would also benefit greatly if the systems sizes could be reduced, making them more mobile and portable.

The GDM concentrations measured during the field study on the Mediterranean Sea were all within the expected area, and seemed to correlate to some degree with the wind force. The average measured GDM level corresponded well with the level measured by the Swedish group’s automated annular KCl coated denuder system. The level measured by the Italian group using tubular denuders was, on the other hand, much lower. In the future, an effort should be made to compare the different methods thoroughly, and to investigate which one of them gives the most accurate GDM measurements.

Validations and testing of for instance efficiency of the denuders, have suffered under the priority of field studies. Then again, have the studies in the field given valuable experiences on problems connected with work outside the laboratory, and how they can be solved.

The question of whether it really is GDM species being collected on the denuders, and to which degree, should be further investigated. No standard reference materials are available for GDM species, making the approach to the problem more complicated. Systems generating GDM from elemental mercury, have been constructed, and an opportunity to test the method on these systems would probably be an interesting approach.

The limits of detection for the method being 2.1 pg (≈ 1 pg/m^3) working in the laboratory, and 8.4 pg (> 4 pg/m^3) working in the field, suggests that major improvements can be made on the field procedures.

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Appendix A

A.1 Calculations and Examples

A.2 Descriptions

A.3 Mercury concentrations

A.4 Gas clock calibrations

A.5 The Mediterranean Oceanographic Cruise

A.6 Simplified electric circuit diagrams

A.7 Photo gallery

A.8 TGM measurements

A.1 Calculations and Examples

A.1 Calculations and Examples

A.1.1 Sample volume and sampling flow

The pumps used for sampling were connected to a gas clock each. The gas clock was counting the litres of air passing by. The total sample volume was the difference between the number on the clocks before sampling and the number after. The gas clocks were calibrated at the instrument laboratory at NILU and the calibration certificates are attached in Appendix 4. The calibration returns a deviation constant, that corresponds how many percents the gas clock is counting wrong. The total sample volume was corrected according to the deviation constant.

Example:
The deviation constant of one of the gas clocks were 5.41. When the sampling started, at 10 am, the gas clock showed 531109.7 litres. When the pump was turned off at 10 am the next day, it showed 535940.2 litres. The measured sample volume was then calculated to be:
(535940,2-531109,7)L = 4830,5 L

The volume had to be corrected according to the deviation constant:
(4830,5 L/105,41%)*100% = 4582,6 L

The pump had been running for exactly 24 hours = 1440 min.

Sampling flow was then:
4582,6 L/1440 min = 3,2 L/min

A.1.2 Calculations of the correct GARDIS calibration constant

The calibration constant on the GARDIS monitor is a programmed value that decides to which degree the signal from the detector is magnified before the result is displayed. The sensitivity of the detector might be reduced as a consequence of pollution or aging. The calibration constant will then have to be increased for the monitor to display the same result as earlier, when the same amount of mercury is present.

Example:
As the sensitivity of the detector may change with the concentration/amount of mercury injected, it was chosen to inject an amount as close to the samples as possible. As the temperature in the room and in the mercury source was 20°C, injections of 2 μL of air saturated with mercury would correspond to 26.352 pg of Hg (according to table in Appendix 3). Initial calibration constant was 300, the sample introduction time was 900 s and the introduction flow was 200 ml/min. The established background value from the system was 2.5 pg (the mean value of the last four background measurements). Six consecutive 2 μL injections were executed and measured. From each displayed value the 2.5 pg background was subtracted, and the magnitude of the signal was calculated as the percentage of the injected amount.

Table A 1: Injections of mercury with initial calibration constant 300. States the injected amount of mercury, the displayed result, the result after correcting for background from the system and the calculated signal magnitude as percentage of injected mercury amount.

Injected(pg)	Measured(pg)	Backg. sub.(pg)	magnitude(%)
26.4	24.1	21.6	81.8
26.4	24.7	22.2	84.1
26.4	24.3	21.8	82.6
26.4	25.6	23.1	87.5
26.4	25.1	22.6	85.6
26.4	24.8	22.3	84.5

The mean of the calculated results in the last column in table A1 was found to be 84.4%. As the calibration constant that gave a 84.4% result was 300, the constant giving 100% was calculated as follows:
(300/84,4%)*100% = 355.5
The GARDIS calibration constant was changed to 355 and another set of injections were performed.

Table A 2: Injections of mercury after changing the calibration constant to 355. States the injected amount of mercury, the displayed result, the result after correcting for background from the system and the calculated signal magnitude as percentage of injected mercury amount.

Injected(pg)	Measured(pg)	Backg. sub.(pg)	magnitude(%)
26.4	28.6	26.1	98.9
26.4	28.1	25.6	97
26.4	29.2	26.7	101.1
26.4	27.9	25.4	96.2
26.4	28.5	26	98.5
26.4	29.3	26.8	101.5

The mean of calculated results in the last column in table A2 was found to be 98.9% with a standard deviation of 2.1%. Considering the deviation, 98.9% was regarded as a satisfying result.

A.1.3 The daily calibrations

When the gold traps and the optical cells in the monitor are quite new, the detector will give a near linearly response in the whole concentration area. The daily calibration could then be performed almost the same way as the adjustment of the calibration constant above.

Example:
Six identical injections of mercury were performed and the displayed signals were compared to the injected amount (percentage). See A.1.2 and Table A1. The mean of the calculated results in the last column in table A1 was found to be 84.4% ±2.1%. The result displayed when a sample was analysed was then thought to be about 85% of the true value, and increased to 100%:
(displayed value(pg)/85%)*100% = Correct sample value

End example

When the gold traps and detector had been used for a while, the response was no longer linear. The example below is one of the daily calibrations made during the field studies at Svalbard, spring of 2001.

Example:
Conditions: Sample introduction time was 900 s, introduction flow 200 ml/min, and the calibration constant 450. Three nearly identical injections of mercury were executed and calculations performed. The results are presented in table A3.

Table A 3: Part one of a daily calibration. Injected mercury amounts, displayed results, results where background is subtracted and signal magnitude relative to injected amount.

Injected(pg)	Measured(pg)	Backg. sub.(pg)	magnitude(%)
16.9	10.8	9.3	55.1
17	10.4	8.9	52.3
17.2	12.1	10.6	61.8

The mean value of displayed signals was 11.1 ±0,9pg and the mean value of the signal magnitudes was 56.4 ±4.9%.

The same kind of injections and calculations were performed for two other mercury amounts, with the following results:
Mean of displayed signals 39.4 ±1.4pg, mean of signal magnitudes 69.6 ±2.6% and mean of displayed signals 88.6 ±2.6pg, mean of signal magnitudes 95.6 ±2.9% respectively.

The means of displayed signals were plotted against means of signal magnitudes, and a regression curve was imposed with aid from the statistic functions in Microsoft Excel. See figure A1 below.

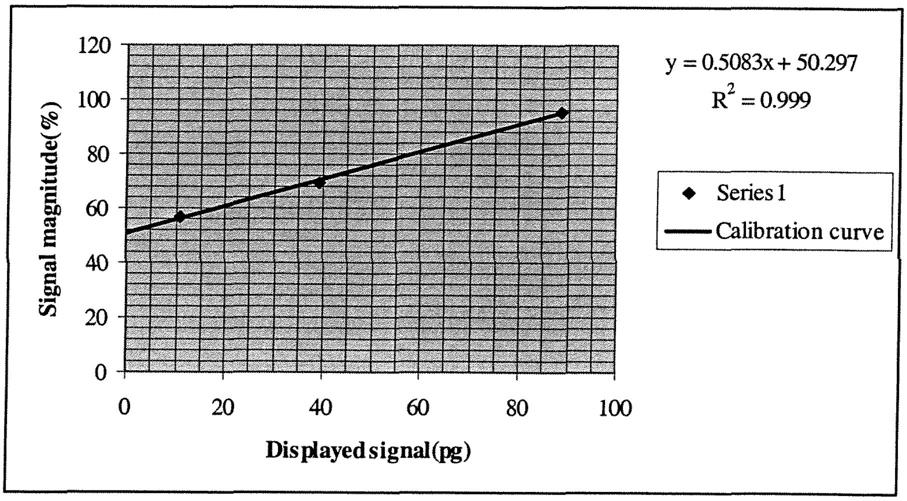


Figure A 1: Calibration curve with regression line. Displayed signals plotted against the signal magnitude relative to injected amount.

Because of the uncertainty in the signal magnitude, the percentage in the figure was rounded to the nearest 5 % when reading of a value. When a signals relative magnitude was determined according to the figure, the value was increased to 100% (see next chapter).

A.1.4 Calculating the sample result

When a calibration curve like the one in figure A1 above, is made, all measured values on the monitor are adjusted according to this. In the example below, were the handling of sample results is presented, the curve in figure A 1 is used.

Example:
The calibration curve in figure A 1 was made early in the morning. The analysing system had a sample introduction time of 900 s, an introduction flow of 200 ml/min and a calibration constant of 450. A stable background value of 1.5 pg was measured. According to the calibration curve, this displayed value is only 50% of the real value. The background was therefore corrected to:
(1.5 pg/50%)*100% = 3.0 pg

The sample denuder was thermally cleaned and the mercury signal from the denuder after cleaning was measured to be 2.1 pg. Corrected value was the:
(2.1 pg/50%)*100% = 4.2 pg

The background from the system was then subtracted and the constant mercury signal from the denuder was calculated to be:
4.2 pg – 3.0 pg = 1.2 pg

The denuder was placed in the sampling box, and the pumps turned on. The sampling continued fro 6 hours. Following the procedure in A.1.1, these parameters were calculated:

Sampling time	: 360 minutes
Sample volume	: 2160 litres
Sampling flow	: 6.0 litres/minute

The sample denuder was immediately analysed. The displayed background from the system was at the time 1.9 pg. Corrected value:
(1.9 pg/50%)*100% = 3.8 pg

The value displayed when the sample was analysed was 26.5 pg. According to the calibration curve, signals of this magnitude represents 65 % of the real value. Corrected result was then:
(26.5 pg/65%)*100% = 40.8 pg

The sampled amount of mercury was then found by subtracting the background from the system (3.8 pg) and the constant mercury signal from the denuder (1.2 pg). Final result was then:
40.8 pg – 3.8 pg – 1.2 pg = 35.8 pg

As the sample volume was 2160 litres = 2.16 m^3 of air, the concentration of mercury in the ambient air was calculated to be:
35.8 pg/2.16 m^3 = 16.6 pg/ m^3

A.1.5 Statistics

Statistic calculations were performed according to J. C. Miller and J. N. Miller, *Statistics for Analytical Chemistry*, Ellis Horwood Limited, Chichester (1993)

A.2 Descriptions

A.2 Descriptions

Type	Specifications	Producer/ supplier	Applications
Activated carbon filter	Gas clean moisture and charcoal filter. High capacity activated carbon and molecular sieves	Chrompack International BV, Middelburg, The Netherlands	Cleaning of zero air during analysis
Adapters, bent glass	Cone to tubing for ground joints NS 19/26, Duran glass	Lenz Laborglas, Wertheim, Germany	Connection between denuders and tubing during sampling, analysis and coating
Beakers	Duran glass, 250 ml	Schott, Mainz, Germany	Container for methanol and KCl. during Coating
Capillary tubing precision bore	Verdia, borosilicate glass	Chance Glass Limited, Worchestershire, England	Restricts the sample introduction flow during analysis
Clean room facilities	USFS 209E class 10 000 (10 000 particles per square feet)	CM Ultraclean, Spydeberg, Norway	Cleaning procedures and coating
Denuder material	SiO_2, quarts glass	QGT – Quarts Glas Technik GmbH & Co, Bad Harzburg, Germany	Quarts material in the custom made denuders
Distilled water	Milli-Q plus water purification system, 220V/50Hz, Compact. Conductivity < 0.5 μS/cm	Millipore Corperation, Bedford, Massachusetts, USA	Cleaning
Electrical heater	Type EHZ 110-265 V 60 W	Pfannenberg Elektro-Spezialgerätebau GmbH, Hamburg, Germany	In sampling box

Type	Specifications	Producer/ supplier	Applications
Electrical heater temperature control	Type ETR Open: 10A, 250V Close: 5A, 250V	Stego Elektrotechnik GmbH, Schwabisch Hall, Germany	In sampling box
Filter holder system, particulate filter	9631 One stage inline	NILU Products AS, Kjeller, Norway	Housing the filter in the analysis system
Gas tight syringes	1800-series, disposable needle, gas tight with handle	Hamilton Bonaduz AG, Bonaduz, Switzerland	Standard injections of saturated Hg-air. Calibration
Gold threads	85/15 - Ag/Pt alloy	Rasmussen, Hamar, Norway	Gold trap in analysis system
Hollow stoppers for ground joints	Blown, Duran glass, NS 19/26	Schott Medica, Wertheim, Germany	Plugging of denuders
Hot plate	Plate made of Ceran®, temperature regulation 50-300°C, Effect 1800W	Gerätewerk Matrei, Matrei am Brenner, Austria	Heating the coating solution
Hydrochloric acid, HCl	Suprapure, 30%	Merck KGaA, Darmstadt, Germany	Br-Cl cleaning solution
Methanol	Pro Analysi	Merck KGaA, Darmstadt, Germany	Coating solution
Needle valve restrictors	Standard 0-16 bar	Bürkart, Farsta, Sweden	Restricts the sampling flow (on pumps)
Particulate filter	Cellulose filter, grade 40, size 47 mm	Whatman International Limited, Maidstone, England	Cleaning of zero air during analysis
Pipette filler	Peleus standard	Deutsch & Neuman, Berlin, Germany	Pulling the coating solution up in the denuder
Plastic clamps for conical joints	Delrin Thermoplastic	Schott Medica, Wertheim, Germany	Plugging of denuders

Type	**Specifications**	**Producer/ supplier**	**Applications**
Polyethylene tubing	Blue polyethylen		Connecting pumps and denuders during sampling
Potassium bromate, $KBrO_3$	Pro Analysi > 99.8%	Merck KGaA, Darmstadt, Germany	Br-Cl cleaning solution
Potassium bromide, KBr	Pro Analysi > 99.5%	Merck KGaA, Darmstadt, Germany	Br-Cl cleaning solution
Potassium chloride salt, KCl	Suprapure	Merck KGaA, Darmstadt, Germany	Coating solution
Quarts beads	Vitreosil clear fused quarts tubing, Flame fused quarts Ingot. Bead size 1-2 mm	Quarts from: Saint-Gobain Quarts PLC, Wallsend, UK Beads prepared by operator	Pyrolysis tube
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	Pyrolysis tube, gold traps and soda lime trap
Sampling inlet shields	High density polyethylen	Dyno Plast Limited, Kongsvinger, Norway	Protecting the denuders from large particles during sampling
Septum	Ice Blue Septa, silicone septum, 9.5 mm	Restek Corporation, Bellefonte, USA	Septum in calibration port on analysis system
Silicon tubing	9*6 mm	Thai Centri Latex AB, Jærfella, Sweden	GARDIS gas inlet and GARDIS flow restriction unit
Soda lime pellets with indicator	Pro Analysi	Merck KGaA, Darmstadt, Germany	Soda lime trap

Type	**Specifications**	**Producer/ supplier**	**Applications**
Teflon connections	PTFE bolt, natural white	Teflon from: Astrup & Sønn, Oslo, Norway Custom made connection at: NILU, Kjeller, Norway	Attach the denuders to the inlet in the sampling box
Teflon grid	PTFE plate, pressed, natural white	Teflon from: Astrup & Sønn, Oslo, Norway Custom made grid at: NILU, Kjeller, Norway	Protect the denuders from particles during sampling
Teflon sleeves for ground joints	PTFE, 0.05 mm	Brand, Wertheim, Germany	Makes connections water- and gas-tight
Teflon tubing	Clear FEP, 1/4"*1/16"	Furon, Mickleton, New Jersey, USA	Tubing for analysis line
Teflon union tee	TFE-Union Tee, 1/4"	Swagelok Corperation, Solon, Ohio, USA	Calibration port and pressure relief unit in analysis system
Tube fittings, brass	Brass 1/4"	Swagelok Corperation, Solon, Ohio, USA	Connecting tubing on inside and outside of sampling box
Tube fittings, steel	316 stainless steel, 1/4" and 1/8"	Swagelok Corperation, Solon, Ohio, USA	Diverse connections in the analytical system
Veneer plates	12 mm veneer plates made of untreated meranti wood	Byggform A/S Malaysia	Material in sampling box
Viton tubing	Fluoroelastomer, Viton, ISO-versinic 6*9 mm	Saint-Gobain Performance Plastics, Charny, France	Dicerse connections in analytical and sampling system

A.3 Mercury concentrations

A.3 Mercury concentrations

The table made by Tekran Inc., Canada, shows the concentrations of mercury per μL saturated air at different temperatures.

Table 6 - Mercury Concentration versus Temperature

deg C	pg/ul	deg C	pg/ul	deg C	pg/ul	deg C	pg/ul	deg C	pg/ul
5.0	3.519	11.0	6.070	17.0	10.232	23.0	16.879	29.0	27.285
5.1	3.552	11.1	6.124	17.1	10.319	23.1	17.017	29.1	27.500
5.2	3.585	11.2	6.179	17.2	10.407	23.2	17.157	29.2	27.716
5.3	3.619	11.3	6.234	17.3	10.496	23.3	17.297	29.3	27.934
5.4	3.652	11.4	6.289	17.4	10.586	23.4	17.439	29.4	28.154
5.5	3.686	11.5	6.345	17.5	10.676	23.5	17.581	29.5	28.375
5.6	3.720	11.6	6.402	17.6	10.767	23.6	17.725	29.6	28.597
5.7	3.755	11.7	6.459	17.7	10.859	23.7	17.870	29.7	28.821
5.8	3.790	11.8	6.516	17.8	10.951	23.8	18.016	29.8	29.047
5.9	3.825	11.9	6.574	17.9	11.044	23.9	18.163	29.9	29.275
6.0	3.860	12.0	6.632	18.0	11.138	24.0	18.311	30.0	29.504
6.1	3.896	12.1	6.691	18.1	11.233	24.1	18.460	30.1	29.734
6.2	3.932	12.2	6.750	18.2	11.328	24.2	18.610	30.2	29.966
6.3	3.968	12.3	6.810	18.3	11.424	24.3	18.761	30.3	30.200
6.4	4.005	12.4	6.870	18.4	11.521	24.4	18.914	30.4	30.436
6.5	4.042	12.5	6.931	18.5	11.619	24.5	19.068	30.5	30.673
6.6	4.079	12.6	6.992	18.6	11.717	24.6	19.222	30.6	30.912
6.7	4.117	12.7	7.054	18.7	11.816	24.7	19.378	30.7	31.153
6.8	4.155	12.8	7.116	18.8	11.916	24.8	19.535	30.8	31.395
6.9	4.193	12.9	7.179	18.9	12.017	24.9	19.694	30.9	31.639
7.0	4.232	13.0	7.242	19.0	12.118	25.0	19.853	31.0	31.885
7.1	4.271	13.1	7.306	19.1	12.220	25.1	20.014	31.1	32.133
7.2	4.310	13.2	7.370	19.2	12.323	25.2	20.175	31.2	32.382
7.3	4.349	13.3	7.435	19.3	12.427	25.3	20.338	31.3	32.633
7.4	4.389	13.4	7.500	19.4	12.531	25.4	20.502	31.4	32.886
7.5	4.429	13.5	7.566	19.5	12.637	25.5	20.668	31.5	33.141
7.6	4.470	13.6	7.632	19.6	12.743	25.6	20.834	31.6	33.397
7.7	4.511	13.7	7.699	19.7	12.850	25.7	21.002	31.7	33.656
7.8	4.552	13.8	7.766	19.8	12.958	25.8	21.171	31.8	33.916
7.9	4.594	13.9	7.834	19.9	13.067	25.9	21.342	31.9	34.178
8.0	4.636	14.0	7.903	20.0	13.176	26.0	21.513	32.0	34.441
8.1	4.678	14.1	7.972	20.1	13.286	26.1	21.686	32.1	34.707
8.2	4.721	14.2	8.041	20.2	13.398	26.2	21.860	32.2	34.975
8.3	4.764	14.3	8.112	20.3	13.510	26.3	22.035	32.3	35.244
8.4	4.807	14.4	8.182	20.4	13.622	26.4	22.212	32.4	35.515
8.5	4.851	14.5	8.254	20.5	13.736	26.5	22.390	32.5	35.788
8.6	4.895	14.6	8.325	20.6	13.851	26.6	22.569	32.6	36.064
8.7	4.939	14.7	8.398	20.7	13.966	26.7	22.750	32.7	36.341
8.8	4.984	14.8	8.471	20.8	14.083	26.8	22.932	32.8	36.620
8.9	5.029	14.9	8.544	20.9	14.200	26.9	23.115	32.9	36.901
9.0	5.075	15.0	8.619	21.0	14.318	27.0	23.300	33.0	37.183
9.1	5.121	15.1	8.693	21.1	14.437	27.1	23.485	33.1	37.468
9.2	5.167	15.2	8.769	21.2	14.557	27.2	23.673	33.2	37.755
9.3	5.214	15.3	8.845	21.3	14.678	27.3	23.861	33.3	38.044
9.4	5.261	15.4	8.921	21.4	14.800	27.4	24.051	33.4	38.335
9.5	5.308	15.5	8.998	21.5	14.923	27.5	24.243	33.5	38.628
9.6	5.356	15.6	9.076	21.6	15.046	27.6	24.435	33.6	38.923
9.7	5.405	15.7	9.155	21.7	15.171	27.7	24.630	33.7	39.220
9.8	5.453	15.8	9.234	21.8	15.296	27.8	24.825	33.8	39.519
9.9	5.502	15.9	9.313	21.9	15.423	27.9	25.022	33.9	39.820
10.0	5.552	16.0	9.393	22.0	15.550	28.0	25.221	34.0	40.123
10.1	5.602	16.1	9.474	22.1	15.679	28.1	25.420	34.1	40.429
10.2	5.652	16.2	9.556	22.2	15.808	28.2	25.622	34.2	40.736
10.3	5.703	16.3	9.638	22.3	15.938	28.3	25.824	34.3	41.046
10.4	5.754	16.4	9.721	22.4	16.070	28.4	26.029	34.4	41.357
10.5	5.806	16.5	9.804	22.5	16.202	28.5	26.234	34.5	41.671
10.6	5.858	16.6	9.889	22.6	16.335	28.6	26.442	34.6	41.987
10.7	5.910	16.7	9.973	22.7	16.470	28.7	26.650	34.7	42.306
10.8	5.963	16.8	10.059	22.8	16.605	28.8	26.860	34.8	42.626
10.9	6.016	16.9	10.145	22.9	16.742	28.9	27.072	34.9	42.949

A.4 Gas clock calibrations

A.4 Gas clock calibrations

The pumps were calibrated against a RITTER TG3 gas clock at the instrumental laboratory at NILU. “Avvik” states the percentage deviation on the gas clock relative to the true volume that has passed. Volumes of air measured on the gas clocks are corrected according to this deviation constant.

Calibrations made on 03.04.00 and on 07.09.00.

Kontroll av tørrgassur på lab

Dato: 03.04.00 Init: TH

Prøveemne		**Referanse**	
Instrument: HG	Nr: 1	Gassur: Ritter	Nr: 13.733
Gassur: REMUS	Nr: 3763632	Type: TG 3	
Tid start:	00.01.00 00:00:00	Tid start:	00.01.00 00:00:00
Tid stopp:	00.01.00 00:16:29	Tid stopp:	00.01.00 00:29:42
Telleverk start:	6830,0 liter	Telleverk start:	463,0 liter
Telleverk stopp:	6947,0 liter	Telleverk stopp:	665,0 liter
		Feilkorreksjon:	1 %
Måleperiode	16,48333 minutter	Måleperiode	29,7 minutter
Total luftmengde:	117,0 liter	Total luftmengde:	202,0 liter
		Liter / time:	408,08 liter/ time
Liter / time:	425,88 liter/ time	Liter / time korrigert:	404,04 liter/ time

Romtemp: ________ °C

Atm.trykk: ________ hPa

Toleranse: 7,00

Avvik: 5,41

Resultat: Gassuret er Ok

Kontroll av tørrgassur på lab

Dato: 03.04.00 Init: TH

Prøveemne

Instrument: H G Nr: 5
Gassur: REMUS Nr: 3763643

Tid start: 00.01.00 00:00:00
Tid stopp: 00.01.00 00:13:15
Telleverk start: 2725,0 liter
Telleverk stopp: 2820,0 liter

Måleperiode 13,25 minutter
Total luftmengde: 95,0 liter

Liter / time: 430,19 liter/ time

Referanse

Gassur: Ritter Nr: 13.733
Type: TG 3

Tid start: 00.01.00 00:00:00
Tid stopp: 00.01.00 00:29:42
Telleverk start: 463,0 liter
Telleverk stopp: 665,0 liter
Feilkorreksjon: 1 %

Måleperiode 29,7 minutter
Total luftmengde: 202,0 liter
Liter / time: 408,08 liter/ time
Liter / time korrigert: 404,04 liter/ time

Romtemp: ________ °C
Atm.trykk: ________ hPa

Toleranse: 7,00
Avvik: 6,47
Resultat: Gassuret er Ok

Kontroll av tørrgassur på lab

Dato: 07.09.00 Init: TH

Prøveemne		**Referanse**	
Instrument: HG	Nr: 1	Gassur: Ritter	Nr: 13.733
Gassur: Remus	Nr: 3763632	Type: TG 3	
Tid start:	00.01.00 00:00:00	Tid start:	00.01.00 00:00:00
Tid stopp:	00.01.00 00:21:02	Tid stopp:	00.01.00 00:35:02
Telleverk start:	8132,0 liter	Telleverk start:	6342,0 liter
Telleverk stopp:	8278,0 liter	Telleverk stopp:	6580,0 liter
		Feilkorreksjon:	1 %
Måleperiode	21,03333 minutter	Måleperiode	35,03333 minutter
Total luftmengde:	146,0 liter	Total luftmengde:	238,0 liter
		Liter / time:	*407,61 liter/ time*
Liter / time:	416,48 liter/ time	Liter / time korrigert:	403,58 liter/ time

Romtemp: 19 °C

Atm.trykk: 991,2 hPa

Toleranse: 7,00

Avvik: 3,20

Resultat: Gassuret er Ok

Kontroll av tørrgassur på lab

Dato: 07.09.00 Init: TH

Prøveemne

Instrument:	HG	Nr:	5
Gassur:	Remus	Nr:	3763643
Tid start:	00.01.00 00:00:00		
Tid stopp:	00.01.00 00:16:57		
Telleverk start:	9297,0 liter		
Telleverk stopp:	9414,0 liter		
Måleperiode	16,95 minutter		
Total luftmengde:	117,0 liter		
Liter / time:	414,16 liter/ time		

Referanse

Gassur:	Ritter	Nr:	13.733
Type:	TG 3		
Tid start:	00.01.00 00:00:00		
Tid stopp:	00.01.00 00:35:02		
Telleverk start:	6342,0 liter		
Telleverk stopp:	6580,0 liter		
Feilkorreksjon:	1 %		
Måleperiode	35,03333 minutter		
Total luftmengde:	238,0 liter		
Liter / time:	*407,61 liter/ time*		
Liter / time korrigert:	403,58 liter/ time		

Romtemp: 19 °C
Atm.trykk: 991,2 hPa

Toleranse: 7,00
Avvik: 2,62
Resultat: Gassuret er Ok

A.5 The Mediterranean Oceanographic Cruise

A.5 The Mediterranean Oceanographic Cruise

Cruise description of the Mediterranean cruise, received from the cruise leader Nicola Pirrone.

PRELIMINARY INVESTIGATION OF EXCHANGE PROCESSES OF ATMOSPHERIC POLLUTANTS AT THE AIR-WATER INTERFACE OVER THE MEDITERRANEAN SEA

PRELIMINARY WORKPLAN

OCEANOGRAPHIC CRUISE: JULY 14-AUGUST 10, 2000

BACKGROUND

The Italian National Research Council (CNR) approved as exploratory grant a research project addressed to investigate air-sea exchange processes of atmospheric pollutants over the Mediterranean Sea. The major focus will be on atmospheric mercury, however, atmospheric measurements of other pollutants (e.g., NOx, SO_2, O_3, metals) will also be carried out. The major aim is to produce a preliminary assessment of air-sea exchange processes of mercury and its spatial variations in the air and sea water of the Med Sea. Based on the results of this preliminary study a research proposal will be prepared for the Mediterranean Sea region in the frame of the Barcelona Convention to which all participants will be invited to take part as partner.

It is useful to point out that studies of air-sea exchange processes of mercury (Hg) are limited to a few measurements performed in open ocean waters and lakes i.e., Kim and Fitzgerald, 1986; Fitzgerald, 1986; Xiao *et al.*, 1991; Lindberg *et al.*, 1995; Baeyens and Leermakers, 1998; Ferrara et al., 2000. The limited data suggest that the (re-) emission is of the same order of magnitude as atmospheric deposition and is thus of great importance when estimating input fluxes to marine environments. Mercury occurs naturally in seawater as Hg°, Hg(II), CH_3HgCl or possibly $(CH_3)_2Hg$ with the Hg(II) species as the dominant form. Particulate Hg forms may also be present. The exchange of these mercury species between the atmosphere and the ocean has not been studied thoroughly or understood. If the ocean waters are supersaturated in any of the volatile mercury species, then there will be a driving force for these species to be emitted to the atmosphere. Chemical or biological processes that convert the dominant sea water species Hg(II) to Hg°, CH_3HgCl and eventually to $(CH_3)_2Hg$, will govern the availability of volatile Hg and thus influence the emission rate from the sea surface.

Preliminary studies carried out in the Mediterranean and Baltic seas show that the contribution of the air-sea exchange in the overall mercury cycle between the atmosphere and sea water can be significant. At present, air-sea fluxes of mercury are computed using simple semi-empirical two-layer models and flux measurements have been performed only in calm wind conditions. Nonetheless, in spite of the paucity of available data, the Baltic and Mediterranean studies have shown that the air-sea flux can be extremely large, and the direction of the flux can alternate from upward to downward depending on the location and meteorological conditions. There is a general agreement in the scientific community that the marine ecosystem can be a sink and/or source of the mercury that is cycling in the global environment, and current estimates of the global mercury budget for the Mediterranean region are affected by high uncertainty. This uncertainty is primarily due to the little progress made so far of the assessment of the role of chemical, physical and biological processes in the water column, sediments, in the top-water micro-layer and in the lower atmosphere above the sea water (air-water interface). The dynamics of water waves (i.e., wave spectra, bubble ejection and sea spray formation) have also been shown to play an important role in the exchange of gaseous and particulate mercury at the air-water interface.

METHODS

The URANIA ship cruise is aimed at carrying out for the first time over-water measurements in the Mediterranean Basin. The goal of this oceanographic campaign is to perform direct flux measurements of atmospheric mercury (and its compounds) in parallel with measurements of the spatial and depth profile variability of dissolved forms of Hg (total Hg, Hg^0 , RGM, Me(Hg), $Me_2(Hg)$ and mercury associated with suspended particolate matter (total Hg and Me(Hg) in the seawater. Furthermore, seawater chemistry parameters (salinity, dissolved oxygen, nutrients, pH, chlorophyll concentrations) will be measured in all water samples. The simultaneous determination of volatile mercury species and other semi-volatile pollutants in the water and in air compartments along with meteorological parameters will also be determined.

In order to achieve the objectives reported above it is proposed to perform the following measurements (see also Table-I) will be performed:

- The actual seawater-air exchange flux of Hg^0 (TGM) will be measured using the Floating Chamber technique or any other methods available at the participant's laboratory.
- Atmospheric profiles above the sea surface of TGM, TPM, RGM and MeHg compounds (MeHg).
- Hg(tot), Hg and MeHg bound to particulates, reactive Hg (Hg_R), dissolved gaseous mercury (DGM), total Hg and MeHg at various depths in the water column, including the top water micro-layer.
- O_3, SO_2, NOx, ions, etc.
- Alogens (i.e., Br_2, Cl_2 and Br Cl, etc)
- Hg(tot), Hg and MeHg bound to particulates, and reactive Hg (Hg_R) in precipitation.
- Seawater chemistry parameters (salinity, dissolved oxygen, DOC, nutrients, particulates, pH, chlorophyll concentrations) will be measured in all water samples using standardised methodologies.

Table I – Proposed Measurements Plan

Specie	**Sampling method**	**Analysis**	**Frequency**
TGM1 (at two heights above the sea)	Tekran	Tekran	Continuous
TGM2	Manual Au	CVAFS	24 hours
TGM3	Gardis	Gardis	Continuous
TPM1	TPM-traps	Thermal desorb.-CVAFS	24 hours
TPM2	MOUDI Impactor,	Acid digest, SnCl2-CVAFS	24/48 hours
TPM4	PM 2.5	Acid digest, SnCl2-CVAFS	24 hours
RGM1	DIC denuder	Thermal desorb.-CVAFS	24 hours
RGM2	Mist chamber (MC)	SnCl2-CVAFS	4-8 hours
Metals	Dicothoms	ICP-MS	24 hours
NOx, SOx, etc.	Annular denuders	Ion chromatography	6-24 hours
Ozone	Analyser		Continuous
Alogens (Cl_2, Br_2, ..)			
Precipitation	Bulk collector	SnCl2- CVAFS	Event
Air-water exchange	Floating Flux chamber		8 hours
Wet deposition Hg	Funnel & bottle	BrCl, Sn(II) reduct.-CVAFS	Events
Hg in the water column at different deeps (dissolved and bound to particles: Hg^0 ,Hg_R, Hg total, Me Hg	Go-Flow bottles	Purging, CVAFS; BrCl, Sn(II) reduct.-CVAFS; Ethylation-GC-CVAFS	
Meteorological data (i.e. wind, T, solar radiation)	Meteorological station		Continuous
Water parameters (i.e. T, salinity)	Portable equipment		Continuous

The same type of parameters can be measured by adopting different alternative methods that are eventually available among the participants. Therefore, methods and type of measurements reported in Table I are only indicative, the participants can propose alternative methods to be used in the frame of an intercomparison exercise to be carried out aboard the RV.

LOGISTIC ASPECTS

The ship cruise is organised by the Institute of Atmospheric Pollution (CNR-IIA) and the Institute of Biophysics (CNR-IB) and will be carried out from July 14 to August 10, 2000 aboard the Research Vessel URANIA. The costs of the cruise are supported by the Italian National Research Council (CNR). The participants will have to support their travel costs included shipping and delivery of their equipment to the RV or at our institute.

The map which follows (Fig. I), shows the ship's cruise that will cover open sea areas as well as coastal areas of the Mediterranean basin for a total of about 2400 nautical miles. The time of the cruise has been split in two groups (GROUP I and II) that will be aboard the RV during two periods each of 14 days in order to allow a replacement/integration of the personnel/participants. The cruise will start from the arbour of Palermo on July 14, 2000 and will end after 14 days in Naples covering roughly 1400 nautical miles in the western basin of the Mediterranean sea. Every day the ship will travel for approximately about 80-120 nautical miles and stop for about 14 hours in order to allow air-sea flux measurements and sampling of the seawater at different depths. Atmospheric measurements will also be carried out while the RV is fixed at a given location. In addition atmospheric measurements will also be performed when the RV travel from one location (see points in the map) to the next one. Nearly 12-14 stops are programmed (the number of stops can be changed if necessary) during the cruise at these locations will be performed air-water exchange measurements as well as water and air measurements.

The second part of the cruise will depart from Naples and will end in Civitavecchia (close to Rome) covering roughly 950 nautical miles in the eastern basin of the Mediterranean Sea. During the cruise are foreseen about 10-12 stops for performing measurements at open sea and coastal sites as well. In order to allow over-water measurements the ship will be travel for 8 hours and will be stop for about 16 hours during the day, with the exception of the stations near the North Sardinia (station n° 22 and n° 23, see on the map) where the RV will stop for a day in order to allow measurements at several coastal spots. The second part will require 14 days including the loading and unloading of equipment and setup of sampling lines. Every group will include 20 scientists for a total of 40 people during the whole cruise period. Table III shows the details of the cruise route included coordinates of the over-water spots at which to perform over-water measurements, starting and ending dates and location of each period.

Table III

Date	Station of sampling	Lat (Nord)	Long (Est)	Kind of sampling *	Embarkation/Disembarkation
14/07/00					Embarkation/Disembarkation from Palermo
15/07/00	1	37° 57' 00	11° 40' 00	Surface water and vertical profiles, air.	
16/07/00	2	37° 00' 00	12° 20' 00	Surface water and vertical profiles, air.	
17/07/00	3	36° 00' 00	13° 35' 00	Surface water and vertical profiles, air.	
18/07/00	4	35° 12' 00	15° 35' 00	Surface water and vertical profiles, air.	
19/07/00	5	34° 35' 00	17° 00' 00	Surface water and vertical profiles, air.	
20/07/00	6	34° 25' 00	19° 00' 00	Surface water and vertical profiles, air.	
21/07/00	7	35° 00' 00	20° 25' 00	Surface water and vertical profiles, air.	
22/07/00	8	36° 10' 00	20° 50' 00	Surface water and vertical profiles, air.	
23/07/00	9	37° 10' 00	20° 30' 00	Surface water and vertical profiles, air.	
24/07/00	10	37° 50' 00	19° 10' 00	Surface water and vertical profiles, air.	
25/07/00	11	37° 55' 00	18° 00' 00	Surface water and vertical profiles, air.	
26/07/00	12	37° 35' 00	16° 35' 00	Surface water and vertical profiles, air.	
27/07/00	13	39° 10' 00	15° 10' 00	Surface water and vertical profiles, air.	Disembarkation to Naples of a part of the first scientific staff.
28/07/00					Embarkation and departure from Naples of a second scientific staff.
29/07/00	14	39° 40' 00	13° 20' 00	Surface water and vertical profiles, air.	
30/07/00	15	39° 05' 00	11° 50' 00	Surface water and vertical profiles, air.	
31/07/00	16	38° 35' 00	10° 25' 00	Surface water and vertical profiles, air.	
01/08/00	17	38° 15' 00	08° 50' 00	Surface water and vertical profiles, air.	
02/08/00	18	38° 20' 00	07° 15' 00	Surface water and vertical profiles, air.	
03/08/00	19	39° 25' 00	03° 00' 00	Surface water and vertical profiles, air.	
04/08/00	20	40° 50' 00	06° 15' 00	Surface water and vertical profiles, air.	
05/08/00	21	41° 25' 00	07° 48' 00	Surface water and vertical profiles, air.	
06/08/00	22	41° 10' 00	08° 30' 00	Surface water and vertical profiles, air.	
07/08/00	22	41° 10' 00	08° 30' 00	Surface water and vertical profiles, air.	
08/08/00	23	41° 21' 00	09° 35' 00	Surface water and vertical profiles, air.	
09/08/00	23	41° 21' 00	09° 35' 00	Surface water and vertical profiles, air.	
10/08/00	24	41°40' 00	11° 00' 00	Surface water and vertical profiles, air.	Arrival and disembarkation to Civitavecchia.

RV URANIA OCEANOGRAPHIC CRUISE

MED-OCEANOR Project

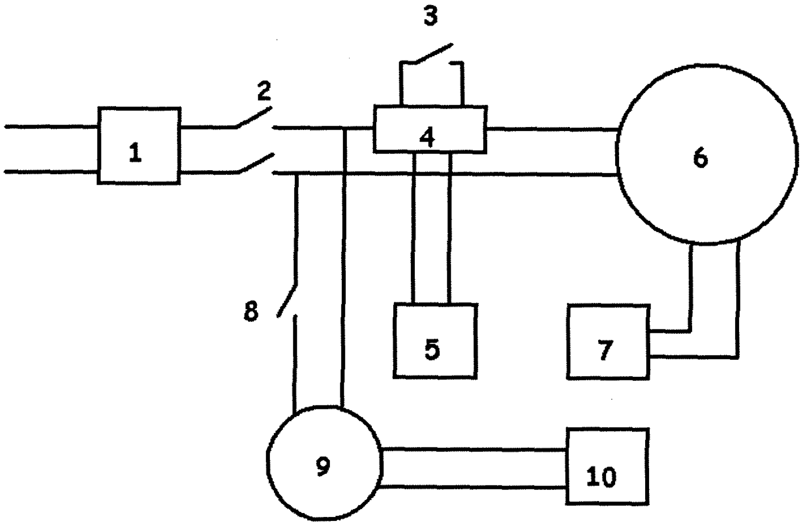
July 14 – August 10, 2000

IIA-CNR

A.6 Simplified electric circuit diagrams

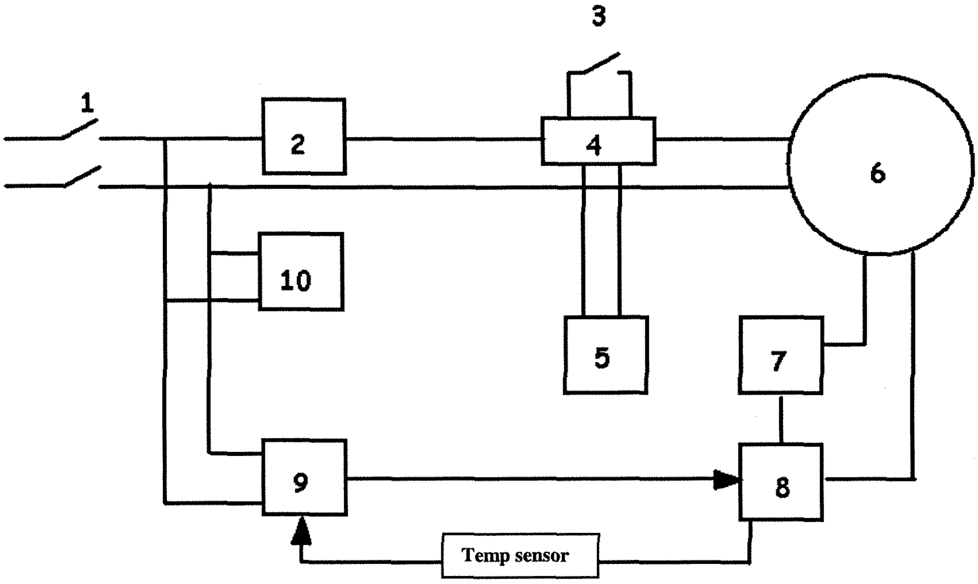
A.6 Simplified electric circuit diagrams

Simplified electric diagrams for both denuder oven versions.



Simplified diagram of first denuder oven with pyrolytic oven.

1. **Mains voltage stabiliser**
2. **Mains power switch**
3. **Denuder oven start switch**
4. **Denuder oven/fan timer**
5. **Fan**
6. **Transformer 600 VA**
7. **Denuder oven**
8. **Pyrolytic oven switch**
9. **Transformer 250 VA**
10. **Pyrolytic oven**



Simplified diagram of second denuder oven with PID-controller.

1. **Mains power switch**
2. **Mains power relay (delayed)**
3. **Denuder oven start switch**
4. **Denuder oven/fan timer**
5. **Fan**
6. **Transformer 600 VA**
7. **Denuder oven**
8. **Denuder oven relay**
9. **PID-controller for 8**
10. **Delay controller**

A.7 Photo gallery

A.7 Photo gallery

Ny-Ålesund, Svalbard

Figure 1: The Zeppelin mountain in Ny-Ålesund. Zeppelin research station close to the top.

Figure 2: The Zeppelin research station (photo: Jan Ivar Tangen).

Figure 3: The view over Ny-Ålesund from the Zeppelin station.

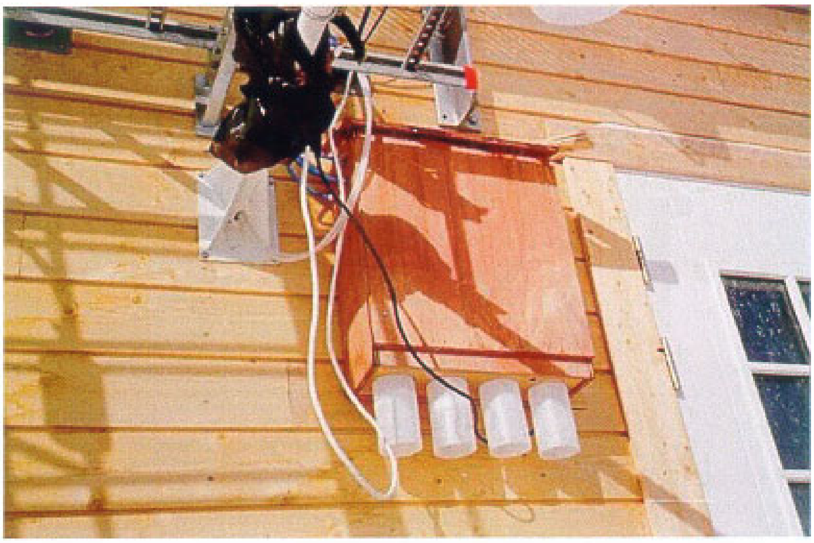


Figure 4: GDM sampling box on the outside wall of the research station.

Figure 5: Analysis system set up at the Zeppelin station.

Figure 6: A lesson on how to exit a cable car in an emergency!

Figure 7: On Svalbard you should always carry a gun outside the settlements, in case you run into a polar bear. Some of us needed some training.....

Figure 8: Beach-party down town Ny-Ålesund, 16th of May 2000.

Figure 9: The confused polar bear who locked himself up in the dog yard 3 o'clock in the morning (photo: Ole Jensen).

Mediterranean Cruise

Figure 10: Analysis set up during the Mediterranean Cruise.

Figure 11: Changing denuders in the sampling box on the upper deck.

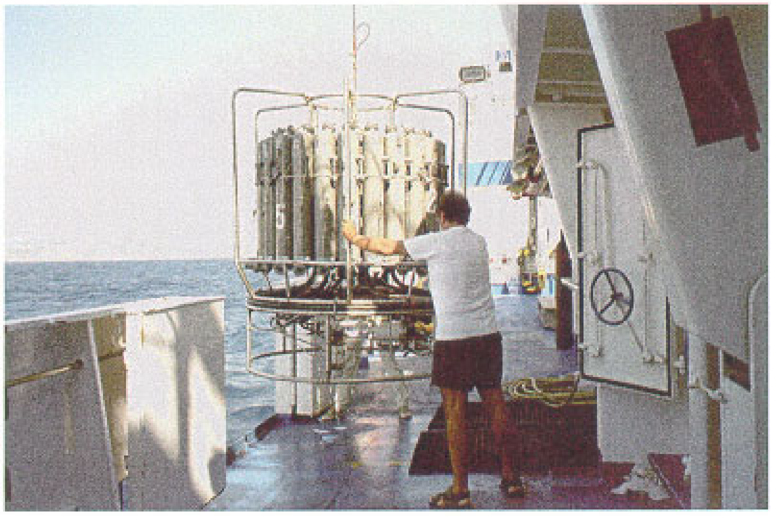


Figure 12: "The Rosetta". Used for sampling of water profiles.

Figure 13: Dinner at the captains table.

Figure 14: Intense research in the Mediterranean Sea!

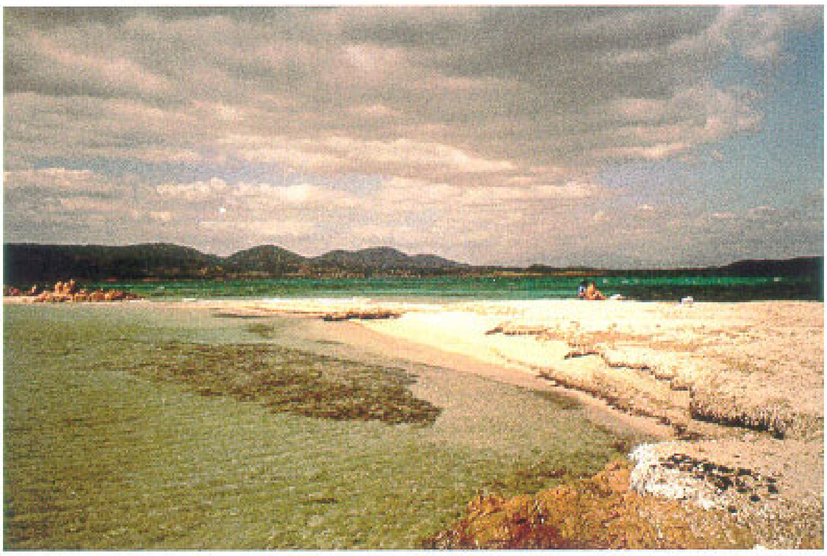


Figure 15: Two hours vacation on the beautiful Tavolara Island.

A.8 TGM measurements

A.8 TGM measurements

The following is a typical series of TGM measurements made by the Tekran monitor placed on the Zeppelin mountain. The final row shows the measured TGM concentrations in ambient air. Sampling flow was about 1.5 L/min, and the sampling time 300 s.

Date	Time	Typ	C	St	at	AdTim	Vol	Bl	BlDev	MaxV	Area	ng/m3
2001.04.19	11:05:00	CONT	A	OK	0	300	7.51	0.204	0.034	0.21	18278	1.098
2001.04.19	11:10:00	CONT	B	OK	0	300	7.5	0.204	0.036	0.21	21165	1.349
2001.04.19	11:15:00	CONT	A	OK	0	300	7.51	0.204	0.034	0.21	20785	1.249
2001.04.19	11:20:00	CONT	B	OK	0	300	7.5	0.204	0.04	0.211	21124	1.346
2001.04.19	11:25:00	CONT	A	OK	0	300	7.51	0.204	0.036	0.211	20330	1.221
2001.04.19	11:30:00	CONT	B	OK	0	300	7.5	0.204	0.031	0.21	20483	1.305
2001.04.19	11:35:00	CONT	A	OK	0	300	7.51	0.204	0.049	0.21	18605	1.118
2001.04.19	11:40:00	CONT	B	OK	0	300	7.5	0.204	0.029	0.211	21253	1.354
2001.04.19	11:45:00	CONT	A	OK	0	300	7.51	0.204	0.028	0.211	20701	1.243
2001.04.19	11:50:00	CONT	B	OK	0	300	7.5	0.204	0.041	0.211	21899	1.395
2001.04.19	11:55:00	CONT	A	OK	0	300	7.51	0.204	0.028	0.211	20784	1.249
2001.04.19	12:00:00	CONT	B	OK	0	300	7.5	0.204	0.039	0.211	22414	1.428
2001.04.19	12:05:00	CONT	A	OK	0	300	7.51	0.204	0.039	0.211	21678	1.302
2001.04.19	12:10:00	CONT	B	OK	0	300	7.5	0.204	0.031	0.211	21097	1.344
2001.04.19	12:15:00	CONT	A	OK	0	300	7.51	0.205	0.037	0.211	22667	1.362
2001.04.19	12:20:00	CONT	B	OK	0	300	7.5	0.204	0.041	0.211	20224	1.289
2001.04.19	12:25:00	CONT	A	OK	0	300	7.51	0.204	0.035	0.211	20077	1.206
2001.04.19	12:30:00	CONT	B	OK	0	300	7.5	0.204	0.035	0.211	20565	1.31
2001.04.19	12:35:00	CONT	A	OK	0	300	7.51	0.204	0.033	0.211	23163	1.392
2001.04.19	12:40:00	CONT	B	OK	0	300	7.5	0.204	0.038	0.211	23321	1.486
2001.04.19	12:45:00	CONT	A	OK	0	300	7.51	0.204	0.037	0.211	22899	1.376
2001.04.19	12:50:00	CONT	B	OK	0	300	7.5	0.204	0.041	0.211	22146	1.411
2001.04.19	12:55:00	CONT	A	OK	0	300	7.51	0.204	0.034	0.211	23706	1.424
2001.04.19	13:00:00	CONT	B	OK	0	300	7.5	0.204	0.033	0.211	21055	1.342
2001.04.19	13:05:00	CONT	A	OK	0	300	7.51	0.204	0.044	0.211	23380	1.405
2001.04.19	13:10:00	CONT	B	OK	0	300	7.5	0.204	0.03	0.211	22417	1.428
2001.04.19	13:15:00	CONT	A	OK	0	300	7.51	0.204	0.029	0.211	23949	1.439
2001.04.19	13:20:00	CONT	B	OK	0	300	7.5	0.204	0.041	0.21	20574	1.311
2001.04.19	13:25:00	CONT	A	OK	0	300	7.51	0.204	0.039	0.211	23842	1.433
2001.04.19	13:30:00	CONT	B	OK	0	300	7.5	0.204	0.038	0.211	22954	1.463
2001.04.19	13:35:00	CONT	A	OK	0	300	7.51	0.204	0.038	0.211	23916	1.437
2001.04.19	13:40:00	CONT	B	OK	0	300	7.5	0.204	0.038	0.211	22076	1.407
2001.04.19	13:45:00	CONT	A	OK	0	300	7.51	0.204	0.029	0.211	24249	1.457
2001.04.19	13:50:00	CONT	B	OK	0	300	7.5	0.204	0.036	0.211	19644	1.252
2001.04.19	13:55:00	CONT	A	OK	0	300	7.51	0.204	0.031	0.212	25852	1.553
2001.04.19	14:00:00	CONT	B	OK	0	300	7.5	0.204	0.04	0.211	21763	1.387
2001.04.19	14:05:00	CONT	A	OK	0	300	7.51	0.204	0.041	0.212	26574	1.597
2001.04.19	14:10:00	CONT	B	OK	0	300	7.5	0.204	0.045	0.211	22680	1.445
2001.04.19	14:15:00	CONT	A	OK	0	300	7.51	0.205	0.045	0.212	24449	1.469
2001.04.19	14:20:00	CONT	B	OK	0	300	7.5	0.204	0.03	0.212	25012	1.594
2001.04.19	14:25:00	CONT	A	OK	0	300	7.51	0.204	0.034	0.212	26649	1.601
2001.04.19	14:30:00	CONT	B	OK	0	300	7.5	0.204	0.032	0.212	26442	1.684

2001.04.19	14:35:00	CONT	A	OK	0	300	7.51	0.204	0.028	0.212	29746	1.787
2001.04.19	14:40:00	CONT	B	OK	0	300	7.5	0.204	0.032	0.212	26050	1.66
2001.04.19	14:45:00	CONT	A	OK	0	300	7.51	0.204	0.047	0.212	26171	1.572
2001.04.19	14:50:00	CONT	B	OK	0	300	7.5	0.204	0.037	0.212	25893	1.65
2001.04.19	14:55:00	CONT	A	OK	0	300	7.51	0.204	0.036	0.212	28115	1.689
2001.04.19	15:00:00	CONT	B	OK	0	300	7.5	0.204	0.031	0.212	26695	1.701
2001.04.19	15:05:00	CONT	A	OK	0	300	7.51	0.204	0.036	0.212	27998	1.682
2001.04.19	*15:10:00*	*CONT*	*B*	OK	*0*	*300*	*7.5*	*0.204*	*0.032*	*0.212*	25842	*1.647*
2001.04.19	15:15:00	CONT	A	OK	0	300	7.51	0.204	0.045	0.212	29120	1.75
2001.04.19	15:20:00	CONT	B	OK	0	300	7.5	0.204	0.043	0.212	26729	1.703
2001.04.19	15:25:00	CONT	A	OK	0	300	7.51	0.204	0.033	0.212	28167	1.692
2001.04.19	15:30:00	CONT	B	OK	0	300	7.5	0.204	0.037	0.212	27517	1.753
2001.04.19	15:35:00	CONT	A	OK	0	300	7.51	0.204	0.04	0.213	29095	1.748
2001.04.19	15:40:00	CONT	B	OK	0	300	7.5	0.204	0.034	0.213	28046	1.787
2001.04.19	15:45:00	CONT	A	OK	0	300	7.51	0.205	0.03	0.213	29421	1.768
2001.04.19	*15:50:00*	CONT	B	OK	0	300	*7.5*	0.204	0.029	0.213	26471	1.687
2001.04.19	15:55:00	CONT	A	OK	0	300	7.51	0.204	0.032	0.213	29046	1.745
2001.04.19	16:00:00	CONT	B	OK	0	300	7.5	0.204	0.037	0.213	27469	1.75
2001.04.19	16:05:00	CONT	A	OK	0	300	7.51	0.205	0.036	0.213	29298	1.76
2001.04.19	16:10:00	CONT	B	OK	0	300	7.5	0.204	0.045	0.212	26382	1.681
2001.04.19	16:15:00	CONT	A	OK	0	300	7.51	0.205	0.034	0.212	26977	1.621
2001.04.19	16:20:00	CONT	B	OK	0	300	7.5	0.204	0.031	0.212	25504	1.625
2001.04.19	16:25:00	CONT	A	OK	0	300	7.51	0.205	0.047	0.213	28760	1.728

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AUTHOR(S) Anne-Kari Valdal	CLASSIFICATION * A CONTRACT REF.

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ABSTRACT

A method for sampling and quantifying gaseous divalent mercury (GDM) has been developed. The method has been applied for GDM measurements during field studies at Ny-Ålesund, Svalbard and over the Mediterranean Sea.

NORWEGIAN TITLE

Utvikling av en metode for prøvetaking og bestemmelse av divalent kvikksølv i gassfase (GDM)

KEYWORDS		
Mercury	Speciation	RGM

ABSTRACT (in Norwegian)

En metode for prøvetaking og analyse av divalent kvikksølv i gassfase (GDM) har blitt utviklet. Metoden er testet i felststudier ved Ny-Ålesund, Svalbard og i Middelhavet.

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