



Measurements of fractionated gaseous mercury concentrations over northwestern and central Europe, 1995–99†

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Although it makes up only a few per cent. of total gaseous mercury (TGM) in the atmosphere, the fraction of oxidised (divalent) mercury plays a major role in the biogeochemical cycle of mercury due to its high affinity for water and surfaces. Quantitative knowledge of this fraction present in mixing ratios in the parts-per- 10^{15} (ppq) range is currently very scarce. This work is based on ≈ 220 data for divalent gaseous mercury (DGM) collected during 1995–99 in ambient air. Over the course of the measurements, the sampling and analytical methods were modified and improved. This is described here in detail and includes transition from wet leaching and reduction procedures to thermo-reductive desorption, the use of annular as well as tubular denuders and adoption of an automated sampling system. The concentration of DGM exhibited a strong seasonal behaviour in contrast to atomic gaseous mercury, with low values in winter and maximum values in summer. The DGM/TGM ratios were frequently found to be below the detection limit ($\leq 1\%$) and in the range 1–5%. A trend of diurnal DGM patterns was observed and implies photolytically induced sources. Scavenging of DGM during rain events was also noticed.

Aim of investigation

Mercury is the only air pollutant predominantly present in atomic form (Hg^0). Owing to high detection sensitivity, it is possible to monitor roughly background sub-ppq concentrations in the atmosphere with direct absorption methods.¹ For oxidised mercury forms present in the parts-per- 10^{15} (ppq) range in ambient air, accumulative sampling is required. Besides CH_3HgX , $(\text{CH}_3)_2\text{Hg}$ and Hg^0 , speciation of gaseous mercury is not obtained, only fractionation. Recently, efforts have been made to determine the fraction of oxidised (divalent) gaseous mercury in the atmosphere.^{2–5} Normally, this is represented by reactive gaseous mercury (RGM). The term is, however, media-dependent and accordingly depends on Hg^{IIa} in the aqueous phase, defined by Brosset.⁶ In the following, divalent gaseous mercury (DGM) will be used instead and only when it is appropriate will the term RGM be given. Even though DGM makes up only a small portion of the total gaseous mercury (TGM) in the atmosphere, it plays an important role in the biogeochemical cycle of mercury in the environment due to its high solubility in water and easy deposition back to terrestrial ecosystems by both wet and dry processes. DGM exhibits dry deposition velocities similar to those of HNO_3 ,⁴ while the corresponding figure for Hg^0 is several orders of magnitude lower. Modelling studies over various spatial scales have shown that even trace amounts of DGM species may control the overall deposition of mercury.^{7,8} However, further advancement of mercury modelling is limited by the lack of data on the mercury composition in the atmosphere.

The earliest evidence for the presence of ppq concentrations of RGM in ambient air was presented by Brosset.⁹ Using a high flow refluxing mist chamber, Stratton and Lindberg^{3,4} were able to obtain diurnal-resolved RGM in ambient air. Representative samples collected corresponded to a detection limit of 1 ppq RGM in ambient air.

Dry adsorption methods to trap oxidised mercury in flue gases rely on the same principle. Oxidised mercury, ' HgCl_2 ', is complexed to $[\text{HgCl}_3]^-$ or $[\text{HgCl}_4]^{2-}$ and retained as the complex anion in a KCl matrix. The diffusion denuder method¹⁰ separates gases from particles based on the fact that they diffuse much faster than particles. For sampling purposes, the gas has to be sucked along a surface that acts as a sink for the specific gas of interest. Numerous coatings can act as a sink for gaseous divalent mercury compounds but not for elemental mercury, such as alkali metal hydroxides, halides and chromates.¹¹ The use of KCl is mainly due to its high deliquescence point. The compound traps DGM compounds such as HgCl_2 and CH_3HgCl .²

We have previously published a paper on the applicability of KCl denuders to sample and determine RGM in ambient air.² In the present paper, a data set of ambient air RGM, DGM and TGM samples from 1995 to date is presented. Over the course of the measurements, the method was modified and improved in order to make the sampling less strenuous and time-consuming and achieve higher time resolution. This includes transition from wet leaching and reduction procedures to thermo-reductive desorption,¹² the use of annular as well as tubular denuders and modifications of the technique aimed at integration and automation. The different techniques are briefly described and commented upon, being used in overlap during transition periods.

Description of experimental procedures

KCl coated denuders

The denuders were made from quartz or borosilicate glass tubes. In addition to tubular denuders ($\varnothing \approx 6$ mm), annular denuders consisting of two coaxial quartz tubes with ≈ 1 mm spacing and with sandblasted annulus walls were also employed. The cleaning of the tubes and application of a methanolic KCl solution to the walls were performed as described previously.² Both ends were cleaned with doubly

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de-ionised water (Millipore, Milli-Q). The effective KCl coated length was 50 and 20 cm for tubular and annular denuders, respectively. The denuders were repeatedly 'blanked' by heating in mercury-free inert gas until low long-term blanks were obtained. Denuders that were to be exposed were generally 'blanked' shortly before collection started.

Determination of mercury

Divalent gaseous mercury. Mercury trapped in the denuders was determined either by leaching or thermal desorption. Borosilicate denuders were only analysed by the former method whereas denuders made from quartz were subject to testing with both methods. The extraction solution, suprapure grade HCl (Merck), was diluted to 1.0 M with Milli-Q water and further purified following the procedure previously described² before being used. Divalent mercury molecules were extracted as their chloro complexes. The leachates were analysed for both RGM and DGM. DGM was obtained after oxidising the leachate with BrCl followed by reduction with $\text{NH}_2\text{OH}\cdot\text{HCl}$ and eventually with SnCl_2 and determined by cold vapour atomic fluorescence spectrometry (CVAFS) (Brooks Rand CVAFS-2 Mercury Analyzer or PSA Millennium Merlin Mercury Analyser). In the former case, a dual amalgamation step was employed.

The set-up used to determine mercury by thermal desorption is described below. During analysis or 'blanking' of the KCl denuder, it was heated externally from a NiCr resistance ribbon. The temperature ($<700^\circ\text{C}$) and time were set to the grade of contamination of the denuder. By desorbing at 450°C , generally $>90\%$ of mercury trapped was released in a few minutes.¹² Samples were generally treated at 450°C for 10 min. Collectors made of borosilicate were also heated to a few hundred degrees to attain low blanks. During sample analysis, mercury species desorbed were pyrolysed before preconcentration on an analytical column with gold-coated quartz beads secured with quartz wool plugs. The pyrolyser consisted of quartz beads in a quartz column maintained at 900°C . The gold trap was heated in a short pulse to 500°C and atomic mercury released was detected by CVAFS (Brooks Rand CVAFS-2 Mercury Analyzer or Tekran 2537A Mercury Vapour Analyzer). The output signal from the detector of the PSA or Tekran instrument was acquired on a portable computer.

Total gaseous mercury. TGM was collected on gold filled quartz tubes (gold traps) either manually or automatically by a field-portable instrument (Ekoservis Gardis-1A or Tekran 2537A Mercury Vapour Analyzer). The gold traps were analysed as described above. Calibration of the instruments was achieved by injecting certain amounts of elemental mercury into the analytical system. Mercury was delivered as acidic aliquots into the PSA instrument and as nitrogen gas saturated with mercury into the other instruments. The Tekran instrument also exhibits an internal calibration system with a permeation source.

Laboratory testing of KCl denuders

A detailed description of the HgCl_2 generation system has been given previously.² The generation rate is highly dependent on the temperature and flow of the carrier gas. The parts of the system upstream of the delivery point have to be completely heated to a temperature exceeding that of the bath to avoid condensation. The composition and stability of the source were tested by connection to an on-line fractionation system normally used for flue gases.¹³ The gas stream was pyrolysed at 600°C in a quartz cell and detected by Zeeman-effect electrothermal AAS (Semtech 2000 Mercury Analyzer) at the same temperature. A few per cent. of elemental mercury was

always present. The generator effluent was then diluted to a suitable concentration by adding carrier gas.

Sampling set-up

The collection efficiency of the divalent species has been shown to be near-quantitative.² Therefore, most of the DGM and RGM measurements were performed with single collectors only. Usually, about $1\text{--}1.5\text{ m}^3$ samples were collected in the KCl denuder. The tubular and annular denuders were maintained at a flow of $0.7\text{--}1$ and $6\text{--}9\text{ l min}^{-1}$, respectively. The denuders were mounted vertically with a downturned funnel at the inlet to protect them from precipitation. In about 60% of the sampling events TGM was co-sampled with DGM.

Manual sampling. The assembly for manual sampling of divalent mercury is given in Fig. 1. Denuders mounted vertically at least 1 m above ground were generally heated at $40\text{--}50^\circ\text{C}$ to avoid KCl deliquescencing during sampling. By having a negligible pressure drop, the volume exposed to the denuder was obtained by simply using a gas meter (Schlumberger) connected downstream.

Automated sampling. An automated sampling system for DGM based on the thermo-reduction desorption principle was also used. The configuration shown in Fig. 2 is generally adopted from the Tekran Model 1130P system (Tekran, Toronto, Canada). A heated (50°C) annular denuder with the effective KCl coated length enclosed in an oven equipped with a cooling fan was used to collect DGM. The denuder was connected with short, cleaned Teflon transfer lines to a pump and CVAFS (Tekran 2537A Mercury Vapour Analyzer) unit. The working principle of the CVAFS system has been described by Schröder *et al.*¹⁴ The surface temperature of the denuder was controlled with a set-point controller (Eurotherm 2416) including time-regulated heating and cooling plug-ins. The flows through the denuder were synchronised with the temperature as well as with the CVAFS unit's sampling cycles using Tekran accessories (1110 Synchronized two port sampling unit, 1120 Standard Addition Controller). This unit was continuously sampling ambient air at 1.5 l min^{-1} . During preconcentration of DGM, when an additional gas flow of $\approx 4.5\text{ l min}^{-1}$ passes through the denuder, the CVAFS unit simply detects Hg^0 . A few cycles before desorption, the inlet of the denuder was blocked with mercury-scrubbed ambient air. Hence, the detector only experienced the influence of

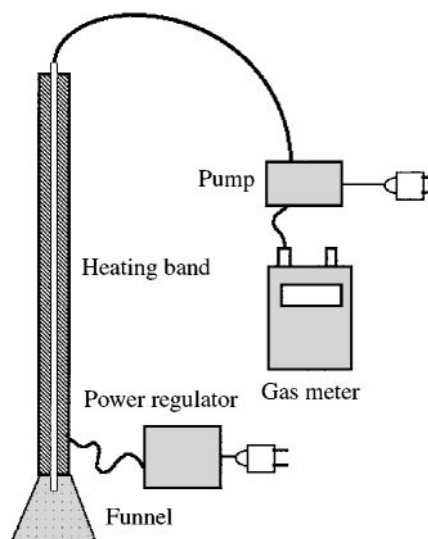


Fig. 1 Schematic diagram of set-up for manual sampling with denuders.

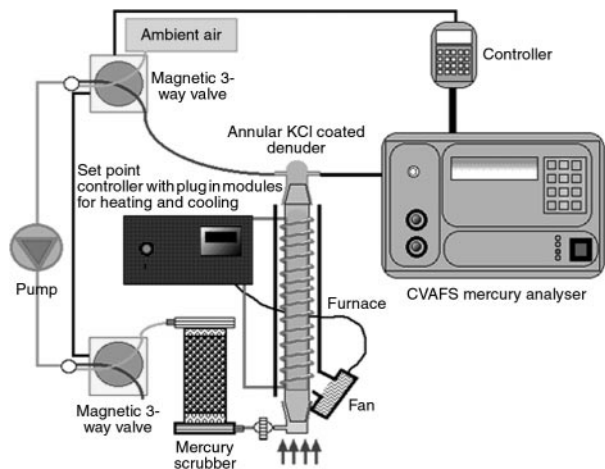


Fig. 2 Schematic diagram of set-up for automated fractionation of gaseous mercury. The flow indicated by the dark-coloured lines to the left of the denuder is active during preconcentration while the flow indicated by the light-coloured lines acts to block the denuder from ambient air during thermal desorption.

mercury zero air. During desorption, the temperature of the denuder was ramped to 450 °C and, consequently, DGM trapped was released, pyrolysed and detected. After the denuder had been allowed to cool down, preconcentration was resumed. The internal blank of the denuder was intermittently checked by passage of mercury zero air during the whole sampling period followed by thermal desorption. In the most recent measurements, deposition of coarse particles on the denuder was prevented by passing ambient air through a cyclone (2.5 µm aerodynamic diameter cut-off).

Sampling sites

Air samples were taken manually from 1995 and automatically since 1998. Sampling was performed during two international intercomparison exercises at Mace Head, County Galway, Ireland, and at Sasseta, Tuscany, Italy, during September 1995 and June–July 1998, respectively, involving groups from North America and Europe.

The sampling sites in Sweden were located around the city of Göteborg (58°N 12°E) situated on the west coast. About 65 samples were exposed at the Brottkärr site 15 km south-west during 1995–97. About 25 samples were collected outside the building of the Department of Chemistry in the urban area of Chalmers. The S:t Jörgen site is located 15 km north, where a combustion simulator is operated with mercury injection for research purposes. Samples were taken outside the simulator building. Measurements of DGM were also performed within the Mercury Over Europe/Mediterranean Atmospheric Mercury Cycling (MOE/MAMCS) Project. MOE/MAMCS is a multi-year project set-up in 1998, which includes air sampling at ten sites in Western and Southern Europe. Some results are reported from the Rörvik site located 35 km south-west of Göteborg.

The locations of the European sampling sites are shown in Fig. 3.

Results and discussion

In the following, the concentrations given were calculated based on the molar weight of atomic mercury; hence, the mixing ratios are slightly overestimated for RGM and DGM. TGM data presented here were averaged to cover RGM/DGM sampling periods.



Fig. 3 Locations of European sampling sites.

Analytical performance of the methods

During 1996, two parallel sampling lines were run with dual leaching analysis and the variations were in the range up to 30%. The DGM method blank is generally 15–35 pg and as low as 10 pg can be obtained for RGM if care is taken to avoid every possible contamination. Leaching of denuders treated with or without repeated heating after a new coating had been applied showed that heating was necessary to eliminate initial contamination. The use of borosilicate tubes, however, prevented high temperatures from being used. As it was a component of all the solutions used, distillation of the suprapure grade HCl from mercury induced by SnCl₂ addition was also found to be important.² Contribution from reagents gives the DGM method a 5–20 pg higher blank compared with that of RGM. The detection limit, based on 3σ of the method blanks, varies between 5 and 15 pg, corresponding to air concentrations of <2 ppq.

The analytical precision of field samples by the thermal method was similar to that described above (5–40% variability, triplicate samples, *n*=7). The regenerative use of thermal denuders makes the blank smaller and less variable without influencing the collection efficiency. Typical values of the blank and detection limit were a few picograms for each based on field blanks. The internal blank of the annular denuder was higher, but could be suppressed to 5–10 pg during automated sampling with repeated heating cycles. The detection limit of the thermal methods corresponds typically to DGM concentrations of <1 ppq.

The sampling data were screened from outliers. Those generally encountered resulted from passivation of gold traps during field measurements and mainly influenced TGM (also DGM during automated sampling), giving reduced concentrations of <100 ppq of the former. About 10% of the automated and <2% of the manually collected RGM/DGM samples were rejected.

Table 1 Summary of mixing ratios of RGM, DGM and TGM obtained in ambient air at European sites, 1995–1999. The values in italic type indicate that most of the single samples grouped together were below the detection limit given in Fig. 4

Site	Season	Method	RGM (ppq)		DGM (ppq)		DGM ^a /TGM (%)	
			$\bar{x} \pm \sigma$	<i>n</i>	$\bar{x} \pm \sigma$	<i>n</i>	$\bar{x} \pm \sigma$	<i>n</i>
Brottkärr	All	Manual leaching	3.4 ± 2.9	45	4.2 ± 4.0	19	1.7 ± 1.6	32
	Summer		4.3 ± 3.1	30	5.0 ± 4.2	15	2.2 ± 1.7	19
	Winter		1.5 ± 1.0	15	1.3 ± 0.6	4	0.8 ± 0.7	13
Rörvik	Winter	Manual heating			2.6 ± 2.4	30	1.1 ± 0.9	20
	Winter	Automated heating			1.0 ± 1.0	34	0.5 ± 0.7	34
	Summer	Manual heating			3.0 ± 3.1	14	1.7 ± 1.8	13
	Summer	Automated heating			3.9 ± 2.1	21	2.5 ± 1.3	21
Chalmers	Summer	Manual leaching	16.0 ± 2.1	3			6.9 ± 2.1	3
	Summer	Manual heating			5.3 ± 2.5	10		
	Winter	Automated heating			1.0 ± 0.4	13	0.4 ± 0.2	13
S:t Jörgen	Summer	Manual leaching	8.7 ± 5.4 ^b	20 ^b				
Mace Head	Summer	Manual leaching	9.1 ± 2.9	4			3.0 ± 0.9	4
Sasseta	Summer	Manual heating			2.1 ± 0.9 ^b	14 ^b		

^aIn Brottkärr data, RGM/TGM is displayed. ^bIncludes duplicate or triplicate exposed samples.

Intercomparison with other methods to determine oxidised gaseous mercury

The methods currently available to fractionate/speciate mercury in ambient air—denuder-based techniques and mist chambers—were intercompared during the start-up phase of the MOE/MAMCS project in Sasseta. Owing to the scarce data set, it was difficult to rank the different methods. However, it can be concluded that they generally produce relatively similar results with variability up to 30–40%. The complete data set including TGM and particulate Hg data will be published elsewhere.¹⁵ The results obtained by manual tubular and automated annular denuders were intercompared during one campaign at Rörvik. The data were significantly correlated ($P < 0.10$, $n = 9$) but differed occasionally in magnitude (within a factor of 2). The results obtained with annular denuders were consistently lower.

Concentrations of RGM and DGM in air

In Table 1, the complete set of over 200 data is categorised into location, season and analytical method. The most extensive data set is from Brottkärr and covers three years, and is displayed in Fig. 4. Exposed denuders were analysed after manual leaching. RGM was determined throughout the whole campaign while DGM was determined occasionally. Samples were usually exposed on a diurnal basis with a flow rate of about 700 ml min⁻¹. The average level of DGM measured was 4.2 ppq compared with 3.4 ppq for RGM. Nineteen of

the samples were analysed for both RGM and DGM. The latter was found to be higher using a one-way analysis of variance test ($F = 0.46$, $P < 0.06$). RGM and DGM were well correlated with each other ($r = 0.92$, $P < 0.0001$) but not with TGM ($P = 0.21$). As shown in Table 1, the difference was more pronounced during the summer period. The RGM fraction is considered to represent inorganic compounds, since even the most stable inorganic mercury compounds in aqueous solution have been found to be easily reduced by SnCl₂. On the other hand, CH₃HgCl(aq) is not reduced by SnCl₂ and does not belong to the RGM fraction.¹⁵ This implies the presence of gaseous monomethylated mercury species in ambient air. However, other methods which can exclusively identify such compounds in air (mist chambers¹⁵ and graphitised carbon traps^{16,17}) have to be used during such speciation.

The concentration of oxidised gaseous mercury exhibited a strong seasonal behaviour ($P < 0.01$) with low values in winter and maximum values in summer. The concentration during the winter period often dropped below the detection limit (1–2 ppq). This trend has also been observed by Lindberg and Stratton⁴ and was attributed to seasonal differences in air stagnation and chemical kinetics. Extensive continental European TGM measurements imply that Hg⁰ is predominantly sink- rather than source-modulated,^{6,9,18–20} which is characteristic of atmospheric trace gases removed by oxidation processes. Higher oxidant concentrations during summer lead to faster oxidation and to a summer minimum of TGM. The intensified oxidation process contributes to increased concentrations of DGM and subsequently enhanced deposition^{21,22} of the highly surface-reactive oxidised mercury forms. However, the role of different photolytically induced gas-phase oxidants has not been shown in any detail.²³ In its extreme manifestation, when high concentrations of oxidants build up during polar sunrise in the Arctic, fast depletion of elemental gaseous mercury occurs.²⁴

During winter periods, the frequency of precipitation increases from 20 to 40% and leads to enhanced scavenging of oxidised mercury. RGM/DGM was measured during three rainfall events during summer 1996 and indeed oxidised gaseous mercury was found to decrease on average by ≈ 60% for both fractions. TGM showed no consistent variation during the same period of time. The limited amount of oxidised mercury collected on the tubular denuders did not allow any diurnal resolution of the measurements. The introduction of high-flow annular denuders enabled the same amount to be collected during a few hours. Fig. 5 shows automated 6 h measurements of DGM and Hg⁰ at the Chalmers site during the shift between January and February 1999 (a data series without any significant passivation of gold traps).

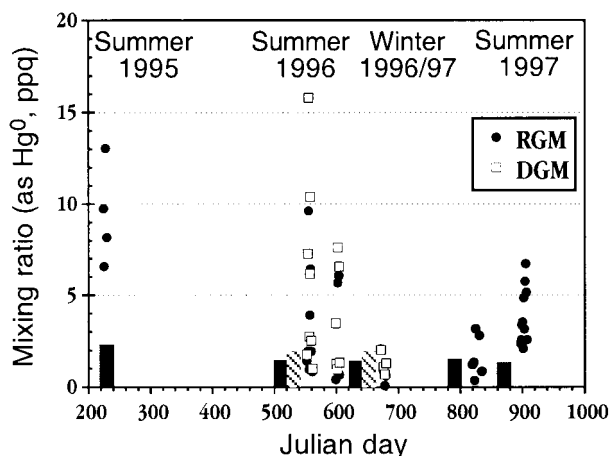


Fig. 4 Time-concentration behaviour of RGM/DGM at Brottkärr during 1995–97. The bars given indicate detection limit for each fraction.

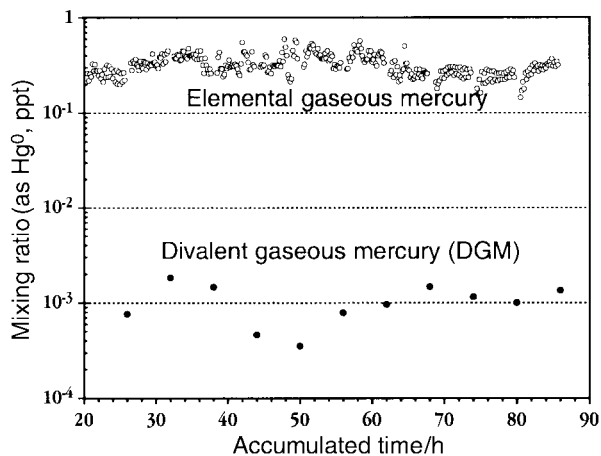


Fig. 5 Fractionation of mercury in air samples at Chalmers during Jan.-Feb. 1999.

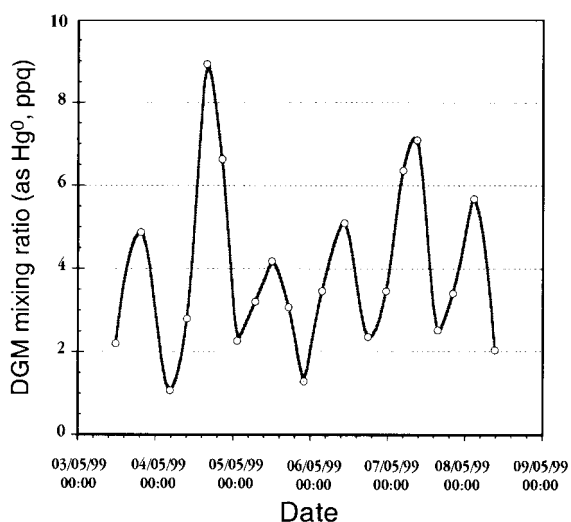


Fig. 6 Diurnal variation in automated DGM samples at Rörvik during 03/05/99–09/05/99.

Lindberg and Stratton⁴ reported higher TGM figures as well as RGM/TGM ratios at temperate latitudes influenced by point sources. High RGM/TGM means similar to those reported in the literature⁴ were obtained in our observations at the urban sites of Chalmers and S:t Jörgen. The main local source of DGM in Göteborg is a municipal waste incinerator. Diurnal cycles with statistically high significance, a factor of >3 between extreme figures, were reported in the US data.⁴ A similar pattern, shown in Fig. 6, was observed at Rörvik during one week in the early summer with prevailing clear sky conditions. Our limited winter data under conditions without precipitation (>75% of a period) did not reveal any highly significant diurnal variation.

The impact of DGM on the deposition of oxidised mercury based on precipitation scavenging has been assessed.⁷ Direct scavenging of a mixing ratio of 5 ppq DGM gives wet deposition concentrations typical for south-west Sweden. As it is highly surface-active, DGM is also likely to influence areas of vegetation significantly by dry deposition. The current database of TGM is now fairly well established, which is

definitely not the case for RGM/DGM. As it is being measured extensively within the MOE/MAMCS campaign and elsewhere, quantitative knowledge of RGM/DGM is, however, likely to be extended in the near future.

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