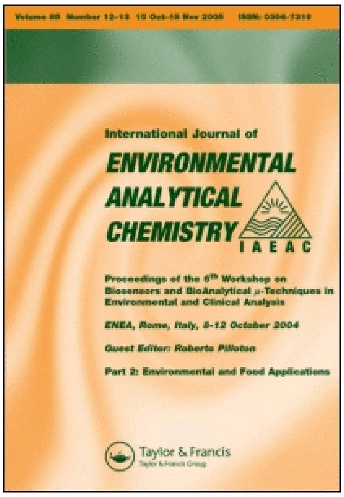

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# Measurements of Reduced Sulphur Compounds in an Industrialized Tropical Region—Cubatão (BRAZIL)

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# MEASUREMENTS OF REDUCED SULPHUR COMPOUNDS IN AN INDUSTRIALIZED TROPICAL REGION—CUBATÃO (BRAZIL)

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Ambient concentrations of $SO_2$, $H_2S$, COS and $CS_2$ have been determined at various sites in the highly industrialized area of Cubatão (Brazil) and in adjacent ecosystems during the years 1990 to 1993. Sulphate has been analyzed in rain samples collected at three sites in the Serra do Mar. The sites are called Vale do Mogi (heavily polluted), Paranapiacaba (moderately polluted), and Vale do Pilões (less polluted). Gas exchange of reduced sulphur compounds between biosphere and atmosphere has been examined with the aid of ambient air enclosures. The investigated sulphur sources (and sinks) were the estuaries south of Cubatão, a reservoir north of Cubatão, and vegetated soils at Vale do Mogi, Paranapiacaba, and Vale do Pilões. The content of reduced sulphur compounds was determined in surface water samples from lakes, rivers, and estuaries in the area under investigation.

Wet sulphate deposition and ambient $SO_2$ concentrations revealed a similar hierarchy of Vale do Mogi, Paranapiacaba, and Vale do Pilões confirming the assumed pollution levels. In addition all investigated sites showed considerably elevated ambient concentrations of $H_2S$, COS, and $CS_2$ when exposed to industrial emissions. Emissions from biogenic sources are dominant over the Billings reservoir and over the estuaries. Flux measurements showed emissions of DMS and $CH_3SH$ from vegetated soils. Deposition or uptake were observed with respect to $H_2S$, COS, and $CS_2$ mainly due to high ambient concentrations of these gases. DMS, COS, and $CH_3SH$ were present in most of the water samples analysed. Maximum DMS concentrations have been detected in anoxic freshwater and estuarine water.

**KEY WORDS**: Reduced sulphur compounds, ambient concentrations, gas exchange, estuaries, freshwater ecosystems, vegetated soils, Brazil.

## INTRODUCTION

During the last decade our knowledge about natural emissions from individual sulphur-producing ecosystems such as oceans[1], coastal wetlands[2,3,4], soils[5,6], forest canopies[7,8,9], and freshwater environments[10] has increased considerably. A limited number of field measurements has been reported from the continents especially from tropical regions[11,7,12]. Only a

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small fraction of authors took into account the regional aspect of the atmospheric sulphur cycle. As recently pointed out[13] concurrent measurements of anthropogenic and biogenic sulphur species are necessary to determine the relative impact of anthropogenic sulphur pollution on the individual environments studied.

In the frame of the world-wide technological development more and more areas in tropical countries are chosen for industrial activities. Most detrimental compounds for the environment of these areas are $SO_2$, $NO_x$, and $NH_3$. Upon entering the atmosphere these compounds may be dissolved in the atmospheric aqueous phase and may also be subjected to oxidation processes in the gas and aqueous phases. Final products like sulphate, nitrate or ammonium return to the earth's surface by wet and dry deposition causing acidification or over-fertilization of soils.

In contrast to $SO_2$, primary emission sources of reduced sulphur compounds like $H_2S$, COS, $CS_2$, DMS, and $CH_3SH$ can be both anthropogenic or biogenic sources. Reduced sulphur compounds are known to be released from fossil fuel combustion, oil refining and paper mills. The global anthropogenic annual emission of short-lived species like $H_2S$, mercaptans, and DMS has been estimated[14] to be in the range of 1–5 Tg(S) $a^{-1}$. An average emission of 0.5 Tg(S) $a^{-1}$ has been calculated [15] for COS and $CS_2$. Sulphur emissions to the atmosphere from natural sources have been recently reviewed by Bates et al.[16].

Figure 1 shows the major pathways of the biogeochemical sulphur cycle.

Two types of biogeochemical pathways are important for the emissions of volatile sulphur species. These are dissimilatory and assimilatory reduction of sulphate. Dissimilatory sulphate reduction which is important mainly for $H_2S$ formation occurs in anoxic sediments of aquatic ecosystems and in anoxic soils. Specialized bacteria are able to metabolize sulphate instead of oxygen. Resultant $H_2S$ may be completely re-oxidized when entering oxygen-rich layers. The incorporation of sulphate into biomolecules like amino acids and their condensation products by assimilatory sulphate reduction is accomplished by living plants and marine algae. Reduced sulphur compounds are exhalated as a consequence of decomposition processes[17] and active release mechanisms of living plants[18]. COS displays two special features which are its photochemical formation in surface water and its uptake by soils and vegetation.

Tropospheric oxidation of the short-lived S(–II) compounds like $H_2S$, DMS, $CS_2$ and $CH_3SH$ leads to $SO_2$, methane sulphonic acid ($CH_3SO_3H$) and COS[19]. In the troposphere the latter compound is inert and may therefore enter the stratosphere where it is photolysed to sulphate. In the troposphere sulphate is also generated by the further oxidation of $SO_2$. The finally produced sulphate re-enters the biosphere by wet and dry deposition.

This atmospheric sulphur cycle has been severely perturbed by anthropogenic activities. Large additional inputs of $SO_2$ and reduced sulphur compounds lead to enhanced sulphate deposition rates. Addition and deposition of sulphate to soils increases the synthesis of sulfur-containing amino acids in microbes[20] and plant foliage[21]. This effect is being enhanced by nitrogen fertilization[22]. Again, enrichment of S-containing amino acids is linked to increasing sulphur gas outputs from live plants and decaying plant debris[23].

In this study we report ambient concentration measurements of relevant S gases carried out at various sites of the Serra do Mar region in Brazil. The exchange of sulphur containing gases between natural environments and the atmosphere has been studied by the aid of flux

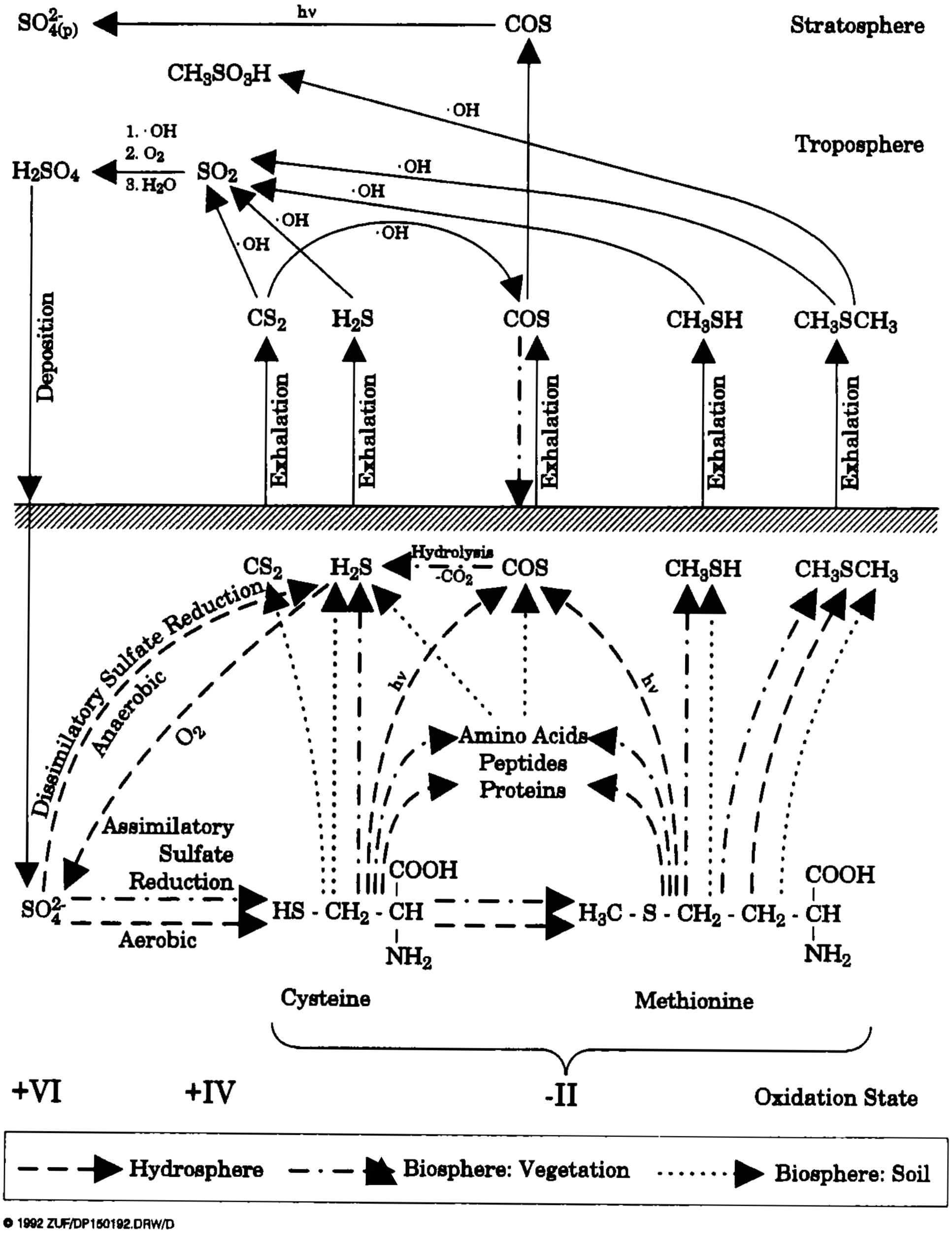

**Figure 1** Scheme of the biogeochemical sulphur cycle.

chambers. Wet sulphate deposition has been measured with rain samplers[24,25]. Reduced sulphur gases were determined in surface water samples.

The highly industrialized tropical area of Cubatão, Brazil, offering a variety of sources of gaseous reduced sulphur compounds within a short distance, was chosen for field research. The main industries are petrochemical and heavy industry, as well as fertilizer, paper, and concrete production. Therefore special emphasis could be given to the question to what extent high deposition rates of $SO_2$, sulphate, and reduced sulphur compounds from anthropogenic sources influence the surrounding natural environments.

The project (ENV 3) is part of a German-Brazilian cooperation in environmental research and technology.

## EXPERIMENTAL

### *Location and climate*

Cubataão is situated in the North of the Santos Basin between Santos and the Serra do Mar (Figure 2; for details see Figure 14). This mountain ridge rises up to 800 m above sea level. and runs parallel to the Brazilian east coast from the state of Rio de Janeiro to Rio Grande

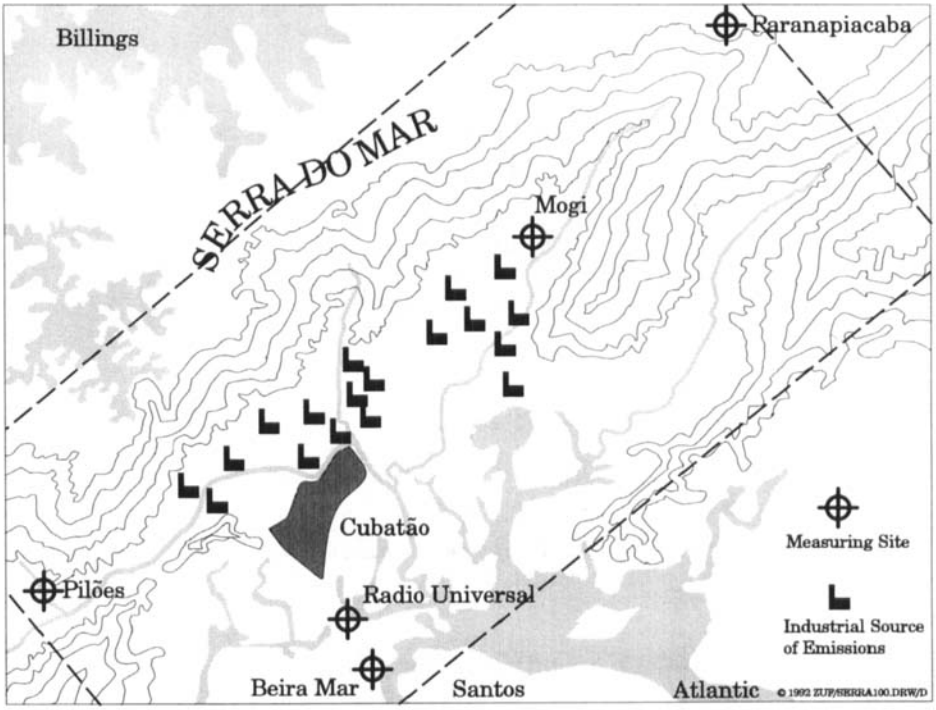

**Figure 2** Map of the area under investigation with the locations of the measuring sites and industrial emission sources indicated.

do Sul. Degraded and non-degraded Atlantic Forest is still covering the Serra do Mar dependent on the influence of industrial pollutants. In the Santos Basin which has a high population density the estuary the Rio Cubatão with its mangrove forests can be found. On the Atlantic Plateau (800–1000 m of altitude) which is separated from the coastal plain by the Serra do Mar the landscape is dominated by a reservoir system called "Billings reservoir". Water from Rio Pinheiros which collects waste water of São Paulo is pumped into the reservoir to maintain a certain water level. The artificial flowing off of the reservoir down the Serra do Mar to the Rio Cubatão is used for power generation. A large industrialized area surrounds Cubatão and extends from the valley of Rio Cubatão in the southwest to the valley of Rio Mogi in the northeast.

The climate of the Serra do Mar is characterized by medium to high temperatures, mist, high humidity, and high rainfall (2500–4000 mm). The local wind conditions are strongly governed by a combination of land and sea breeze and mountain and valley wind.

### *Measuring sites*

In order to perform detailed studies of the atmospheric chemistry in the area of Cubatão three measuring sites were selected. They are indicated in Figure 2. The first station is situated in the valley of Rio Mogi at an area which belongs to Bayer do Brasil (Mogi station, elevation 20 m). The second station is located in the biological reserve of Paranapiacaba close to the spring of the Mogi river (Paranapiacaba station, elevation 860 m). The third station is situated in the valley of Rio Pilões (Pilões station, elevation 40 m). All stations are equipped with measuring houses which contain instruments for continuous monitoring of atmospheric concentrations of $SO_2$ (Pulsed Fluorescence, Thermo Environmental, Model 43 A), $O_3$, NO, and $NO_2$. Meteorological parameters like wind speed, wind direction, temperature and humidity are also monitored continuously. Each station is also equipped with a wet-only rain collector. The rain is sampled in a one week's period. The subsequent analysis of the rain samples is done by the laboratories of the Companhia de Tecnologia de Saneamento Ambiental (CETESB) in São Paulo.

An ancient road (Caminho do Mar) which nowadays is closed for private traffic has been utilized to determine ambient concentration gradients of reduced sulphur compounds along the slope of the Serra do Mar.

Two research flights were conducted in the atmosphere over Cubatão to measure the vertical distribution of reduced sulphur compounds.

In order to investigate the gas exchange between vegetated soils of the Serra do Mar and the atmosphere three sites were chosen which are also included in the research activities of soil scientists and botanists. The site in the biological reserve of Paranapiacaba is located in direct vicinity to the measuring houses. In the valley of Rio Pilões a site was chosen about 1 km northwest of the measuring house at an area which pertains to the state company for production of drinking-water (elevation 150 m). Since no forest can be found close to Mogi station a site at the slope of the Serra do Mar (elevation 250 m) was chosen for the chamber experiments.

The vegetation cover at the three sites mirrors the exposition to different pollution levels. Whereas the Atlantic Forest at the Mogi site has been replaced by secondary pollution tolerant tree species original vegetation can be found around Paranapiacaba station. Nevertheless the rain forest in the biological reserve of Paranapiacaba is affected by pollution as can be seen from significantly reduced biological diversity[26]. In the region of the Pilões river degradation is limited and a highly diversified arboreal vegetation can be observed[27].

### *Applied analytical methods*

*Gas Chromatography.* Reduced sulphur compounds like $H_2S$, COS, $CH_3SH$, DMS, and $CS_2$ are determined discontinuously. They are sampled by quartz glass traps immersed in liquid argon. For subsequent analysis gas chromatography with a flame photometric detector is applied. The desorption of the sulphur compounds is accomplished in a two step process (–78 °C and 25 °C). The subsequent gas-chromatographic separation is done at 0 °C and 60°C, respectively. The temperature of the analytical column is controlled by Peltier elements. The analytical procedure has recently been described in detail[28]. A scheme of the analytical set-up is shown in Figure 3. By the aid of mobile sampling units discontinuous sampling for gas-chromatographic analysis was done at various sites in the Cubatão area in order to discover main sources for the different reduced sulphur gases. Intensive simultaneous sampling was done in the Mogi Valley and along the Caminho do Mar.

*Calibration.* The analytical instruments are calibrated under field conditions close to the measuring sites. Figure 4 shows a scheme of the calibration system for the gas chromatograph. The scheme comprehends three sections, which are named clean air unit, permeation unit and dilution unit.

Clean air is generated by purging ambient air. It is filtered by silica gel, activated charcoal and a fraction of molecular sieve with 5 and 10 Ångstrøm.

The permeation unit is designed as a two chamber system with a proportional temperature control providing a constant temperature of 30 °C. The temperature drift is less than ± 0.1 °C. Each chamber contains a permeation tube. It is certified that the variabilities of the permeation rates are less than 5% (NBS-Certificate). Pure nitrogen is used as carrier which transports (50 ml $min^{-1}$ for each chamber) the permeated traces of the respective gases to the dilution system. The gas chromatograph is calibrated by samples of undiluted gas which leaves the permeation unit. For this purpose a septum is provided which allows the uptake of a gas sample by a syringe. The gas mixture is further diluted in a two step gas dilution system. By the aid of this system it is possible to provide concentrations of gas blends in the ppt range. Cryo samples of the diluted gas can be taken to calibrate the sampling system.

### *Dynamic exchange chambers*

For a direct determination of mass fluxes between atmosphere and biosphere dynamic exchange chambers have been designed (Figure 5). They consist of three parts which can easily be connected and installed in the field. For flux measurements in terrestrial ecosystems cylindrical stainless steel rings are provided as foundations. They are inserted in the soil to remain there for several years. The side walls of the cylindrical chamber are provided by a

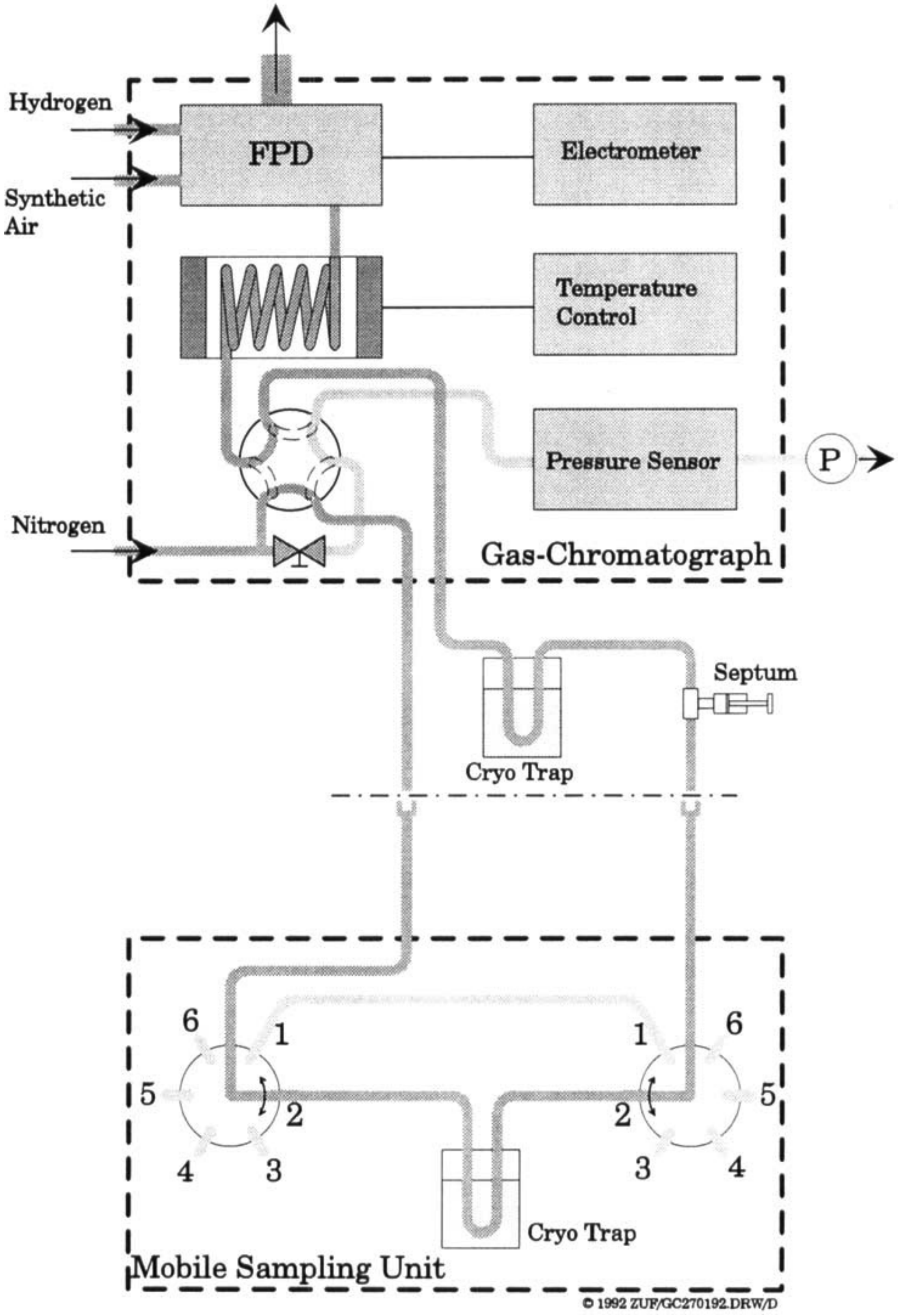

**Figure 3** Scheme of the gas chromatographical system. A mobile sampling unit is provided for external sampling in the field. The sampling unit can be connected to the gas chromatograph. For the analysis the sample is preconcentrated in a capillary loop.

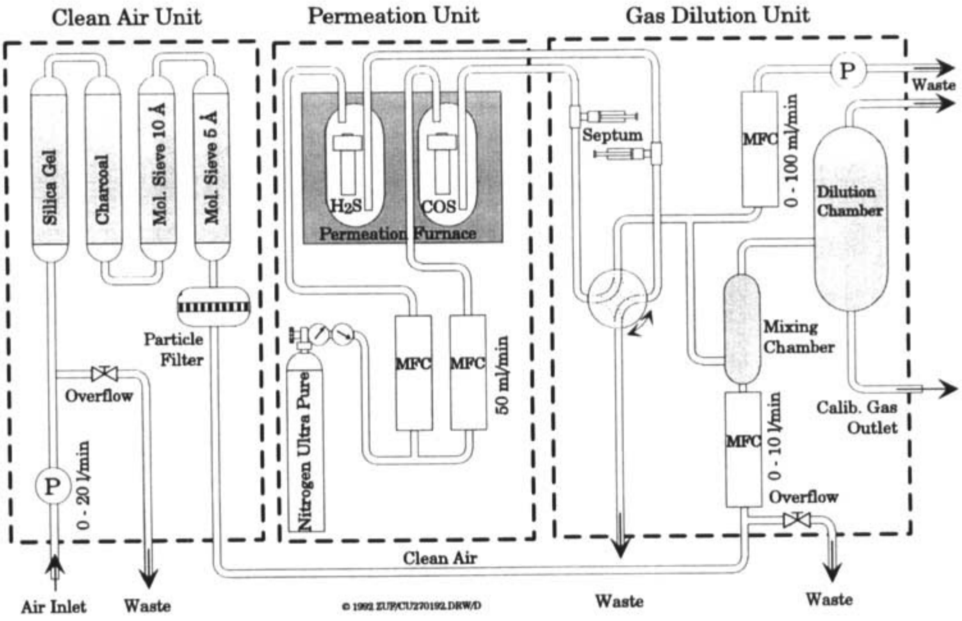

**Figure 4** System for the calibration of the instruments used for the detection of sulphur compounds (MFC = mass flow controller).

hose of transparent FEP teflon film (0.025 mm thickness). It is in situ fixed to the foundation and to the top of the chamber. This chamber top is made out of clear Plexiglas and comprises an air inlet and outlet together with a fan which passes ambient air through the chamber. Ambient air as sweep gas was chosen since sulphur-free enclosures cannot measure natural uptake and data obtained from this sampling method are likely to be overestimates of natural fluxes[29]. The incoming air is first lead to the bottom of the chamber by the aid of a FEP teflon tube which is attached to the air inlet. In aquatic ecosystems the steel foundation is replaced by a teflon ring. Its weight keeps the lower end of the chamber under the water surface. During low tide (estuaries) the teflon ring was slightly depressed in the mud to ensure good seal. With the regulable fan chamber flush rates between 80–800 L min$^{-1}$ are achieved. For the investigation of weak sulphur sources the flow rate had to be reduced to 3–13 L min–1 by diameter reduction of inlet and outlet tubes.

Flux data were obtained by taking simultaneous cryo samples from the inlet and outlet of the dynamic flux chambers. The flux is calculated from the concentration difference between the inlet and outlet of the chamber, the chamber flush rate, and the enclosed surface area.

When the chamber technique was applied on the Billings reservoir the chamber had been mounted on shipboard.

Two permanent steel foundations, one in the open field and one in the forest, have been installed at Vale do Mogi, Paranapiacaba and Vale do Pilões, respectively.

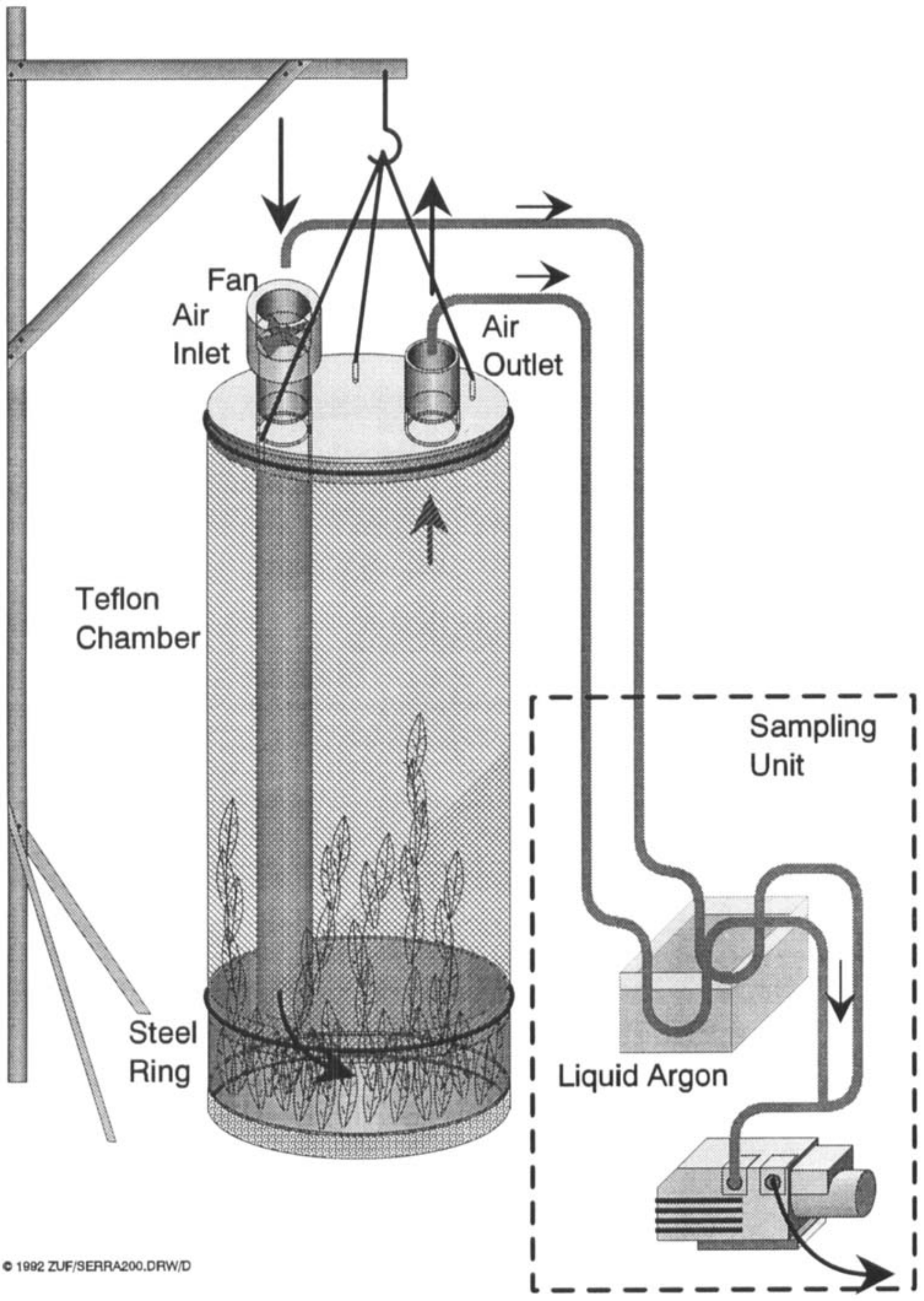

**Figure 5** Scheme of the dynamic exchange chamber for the determination of sulphur mass fluxes from and to aquatic and terrestrial ecosystems.

### *Purge and trap analysis of water samples*

A purge and trap method has been adopted to analyse water samples for their contents of reduced sulphur compounds[30]. Water samples of 40–50 ml volume were flushed with nitrogen under vacuum. The emanating gas was trapped in a quartz glass loop cooled with liquid argon. After preconcentration the trapped sample was subjected to gas-chromatographic analysis. The pH of the sample had not been adjusted to volatilize $H_2S$.

## RESULTS AND DISCUSSION

### *Wet deposition of sulphate*

From December 1990 to April 1991 during a period of twenty weeks rain samples were collected at the stations Mogi, Paranapiacaba and Pilões. The duration of the sampling was always one week. At Paranapiacaba station electric power was only available until the end of February 1991. Therefore analytical data of only ten samples could be obtained from this station.

In Table 1 mean values of the concentration of $SO_4^{2-}$ calculated from the measured data are given[24,25]. Samples collected at Mogi station show the highest concentration of sulphate. In contrast to the Mogi station the content of sulphate in the rain samples collected at Paranapiacaba and Pilões station is less by a factor of three. In addition Table 1 shows the mean precipitation height at all three stations and the resulting values of the wet sulphate deposition. They are in the range between 0.25 and 1.01 mmol $m^{-2}$ $d^{-1}$. These are rather high values compared to deposition fluxes measured in Central Europe. For instance in the area of Frankfurt/Germany one gets only 0.058 mmol $m^{-2}$ $d^{-1}$ as a mean value of the wet deposition of sulphate[31]. In the Amazon Basin wet deposition fluxes of 0.012 mmol $m^{-2}$ $d^{-1}$ (dry season) and 0.011 mmol $m^{-2}$ $d^{-1}$ (wet season) have been found[7,8]. The relatively high value of the wet deposition of sulphate is a first indication of a heavily polluted atmosphere in the area of Cubatão. Up to now no information about the dry deposition of sulphate is available.

**Table 1** Sulphate concentrations in rain water, precipitation, and resultant wet sulphate deposition at three sites of the Serra do Mar.

| Station | $SO_4^{2-}$ Concentration ($\mu$mol/L) | Precipitation (L/$m^2$d) | $SO_4^{2-}$ Deposition (mmol/$m^2$d) |
|---|---|---|---|
| Mogi | 95.3 | 10.6 | 1.01 |
| Paranapiacaba | 30.5 | 12.2 | 0.37 |
| Pilões | 22.7 | 11.2 | 0.25 |

### *Ambient concentration measurements*

*SO2.* Ambient $SO_2$ concentrations have been measured more or less continuously at all three measuring stations from December 1990 up to now. Diurnal variations of $SO_2$ ambient concentrations have been averaged over periods of 15 to 30 days during March (summer) and September (winter) 1992 for all three measuring stations. The data of the winter period are shown in Figure 6. At all three locations maximum concentrations occur between sunrise and noon owing to the exposition of the stations to industrial emissions under sea breeze conditions. Mean and maximum diurnal $SO_2$ concentrations averaged over each of the both periods are presented in Table 2. Ambient $SO_2$ concentrations at the three stations reveal the same hierarchy as the wet sulphate deposition. With one exception daily mean and maximum concentrations at Mogi are 3 to 7 times higher than at Paranapiacaba or Pilões station. The only marked difference between summer and winter data can be observed at Pilões station. The mean daily concentration maximum at Pilões station is almost ten times higher in March than in September and is in the same order as at Mogi station. The wind sector between 45°

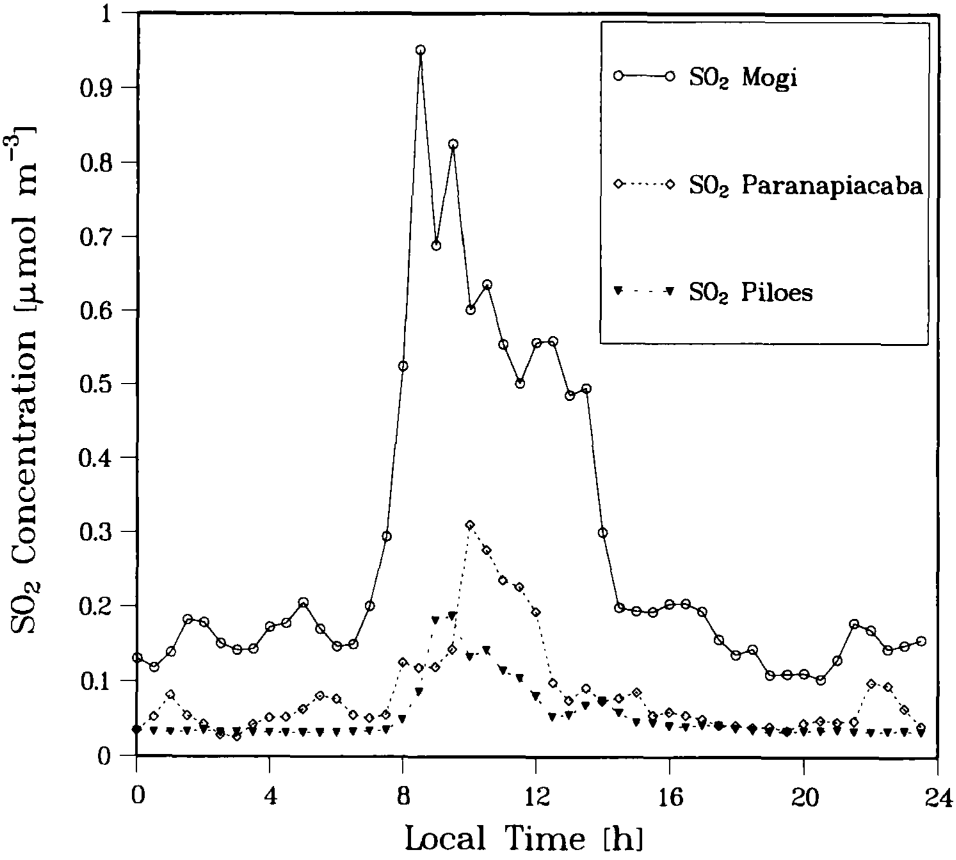

**Figure 6** Mean diurnal variation of ambient $SO_2$ concentrations at three sites of the Serra do Mar in winter (September 1992).

**Table 2** Mean diurnal $SO_2$ concentrations during two periods in 1992 at three sites of the Serra do Mar.

| Station | Mean diurnal $SO_2$ Concentration ($\mu$mol/m$^3$) | | | |
|---|---|---|---|---|
| | February 28 - March 30, 1992 | | August 28 - September 15, 1992 | |
| | Diurnal mean | Diurnal maximum | Diurnal mean | Diurnal maximum |
| Mogi | 0.30 | 1.06 | 0.27 | 0.95 |
| Paranapiacaba | 0.14 | 0.28 | 0.08 | 0.31 |
| Pilões | 0.11 | 1.01 | 0.05 | 0.14 |

and 135° has been chosen to be responsible for elevated ambient $SO_2$ concentrations at Pilões station. This wind sector has a frequency of 31 % in March and only 7 % in September probably as a result of the reduced local circulation during winter months.

*H2S, COS, and CS2.* In Figure 7 typical diurnal ambient concentration variations of the sulphur gases $H_2S$, COS, $CS_2$ and $SO_2$ at Mogi and Paranapiacaba station are shown together with meteorological data. The concentration is highly variable and strongly governed by the local wind circulation. Between sunrise and noon when the wind is changing its direction by 180 degrees both stations become situated downwind to the industrial emissions and a pronounced maximum in sulphur gas concentrations can be observed. This ambient concentration maximum at Mogi is lower (March 30) under stronger sea breeze conditions (wind speed 3–4 m $s^{-1}$) than under conditions of limited circulation (March 31, wind speed 1–2 m $s^{-1}$). A second observation that can be made is that low wind circulation (March 31) leads to significant concentration gradients between Mogi and Paranapiacaba whereas on March 30 maximum ambient concentrations during sea breeze (225°) are in the same range at both stations. During land breeze/mountain wind (45°) ambient concentrations approximate background levels.

After a few spot check measurements in 1991 the large petrochemical complex (Petrobras-RPBC) between Cubatão and the slope of the Serra do Mar (Caminho do Mar) had been expected to be the main source of reduced sulphur compounds in the region as it had already been documented for $SO_2$ (6120 t $a^{-1}$, 34% of total $SO_2$ emission)[32]. To confirm this in detail measurements down-wind of the refinery had to be performed. This has been realized during sea breeze with gradient measurements along the Caminho do Mar (Figure 8) and during land breeze by aircraft measurements in the atmosphere over Cubatão (Figure 9). Vertical profiles along the Caminho do Mar during sea breeze (Figure 8, right side) reveal increasing ambient concentrations of $H_2S$, COS, and $CS_2$ with decreasing altitude indicating a common source at altitudes below 450 m. The same gradients can be observed during land breeze in the atmosphere over Cubatão (Figure 9, left side), whereas both low ambient concentrations and weak gradients have been detected over Mogi Valley (Figure 9, right side).

The influence of another important source of reduced sulphur gases on the Cubatão area could be demonstrated during land breeze. The obtained vertical profile along the Caminho

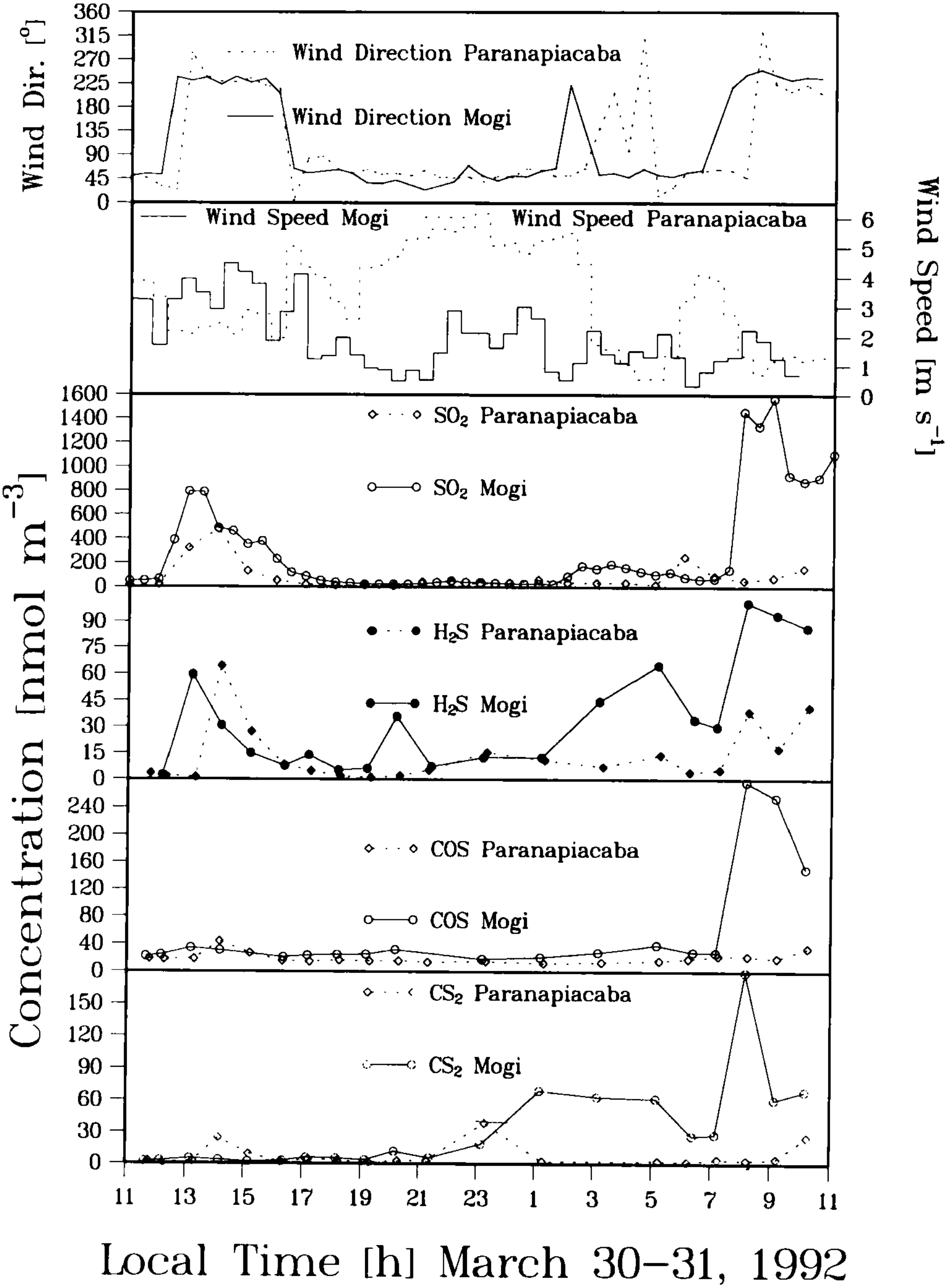

**Figure 7** Diurnal variation of $SO_2$, $H_2$, COS and $CS_2$ concentration, wind speed, and wind direction at two sites in the Mogi Valley in March 1992.

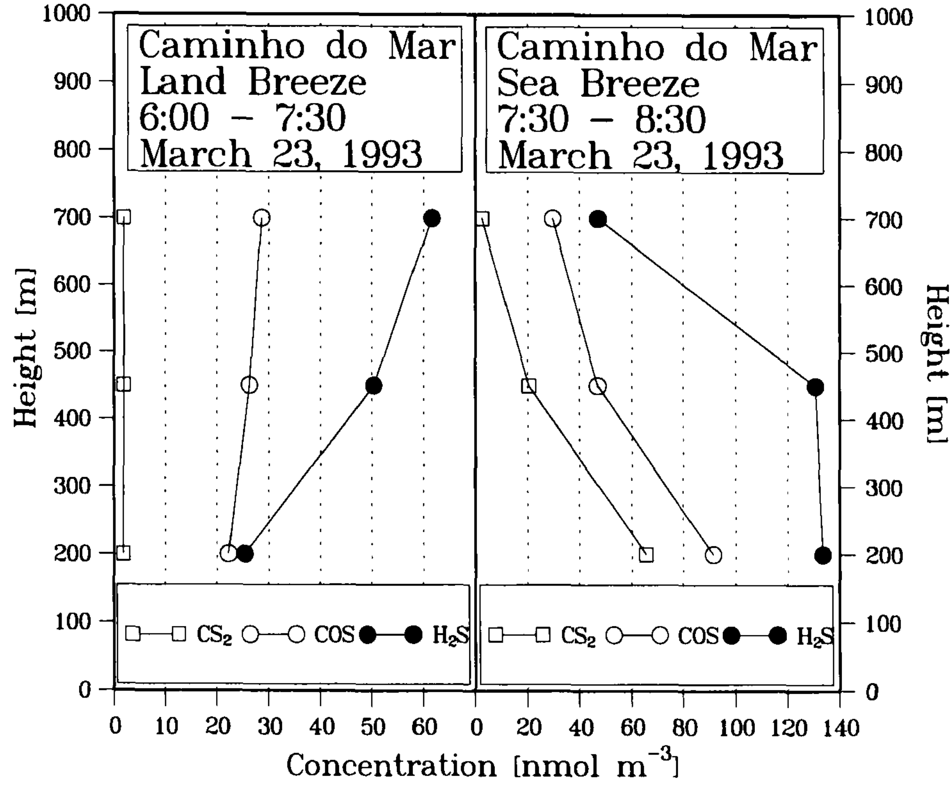

Figure 8 Vertical profiles of $H_2S$, COS, and $CS_2$ concentrations along Caminho do Mar during land and sea breeze on March 23, 1993.

do Mar during land breeze (Figure 8, left side) shows increasing ambient $H_2S$ concentrations with increasing altitude indicating a source on the Atlantic Plateau. Obviously this source is dominated by $H_2S$ emissions since COS and $CS_2$ show weak or not significant gradients. A well-known $H_2S$ source on the Atlantic Plateau is the anoxic part of the Billings reservoir.

A correlation analysis has been executed for ambient concentration data obtained from Mogi and Paranapiacaba station (Table 3) and from vertical profiles at the Caminho do Mar (no $SO_2$ data available). In general good correlation between $SO_2$ and reduced sulphur compounds can be seen from the data ($r > 0.5$, $n = 32–75$) owing to common anthropogenic sources. Best correlation with $SO_2$ has been found for $H_2S$ at Mogi station ($r = 0.76$, $n = 56$). The dominating $SO_2$ source in Mogi Valley is COSIPA steel-works (4436 t $a^{-1}$, 25 % of the total $SO_2$ emission)[32] which is located south of the measuring site. In the same region a strong smell of $H_2S$ of unknown origin is often perceivable.

Correlation between COS and $CS_2$ is high at both stations ($r > 0.75$, $n = 37,46$) and highest at Caminho do Mar ($r = 0.97$, $n = 24$) in direct vicinity to the presumed main source of these two compounds.

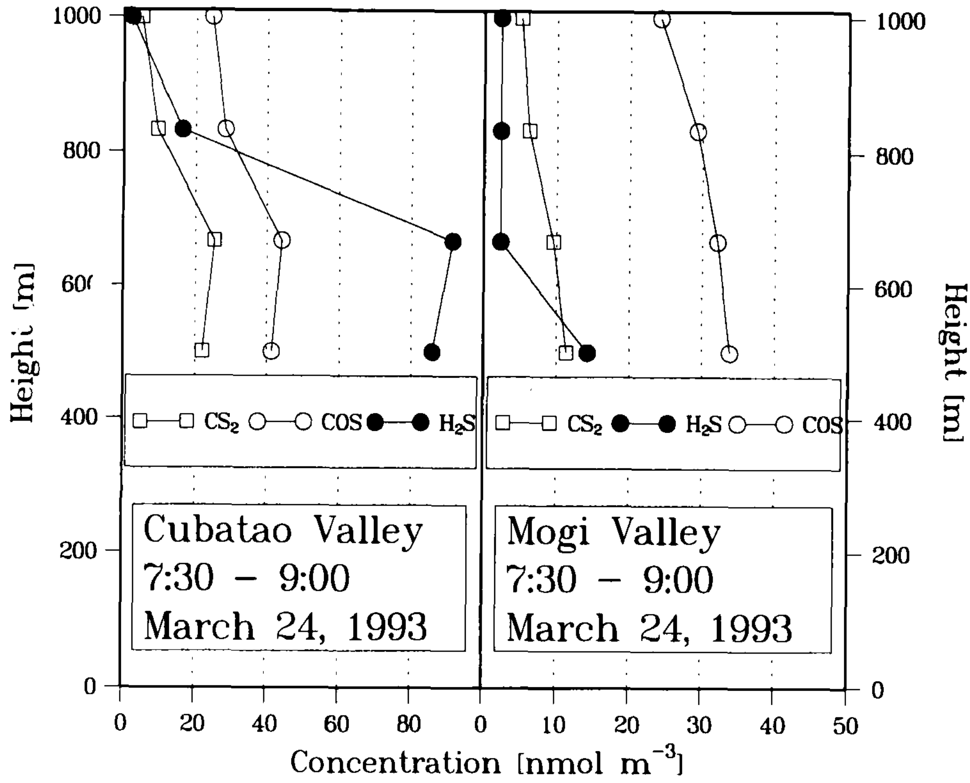

**Figure 9** Vertical profiles of $H_2S$, COS, and $CS_2$ concentrations in the atmosphere over Cubatão and Mogi Valley during land breeze on March 24, 1993.

Dimethyl Sulphide could only be detected during night-time and early morning hours when vertical mixing and photochemical oxidation should be lowest.

**Table 3** Correlation coefficients of regressions between ambient concentrations of $SO_2$, $H_2S$, COS, ad $CS_2$ at two sites in the Mogi Valley (n = number of samples).

| | $SO_2$ | $H_2S$ | COS | $CS_2$ | Mogi |
|---|---|---|---|---|---|
| $SO_2$ | ------------------ | r = 0.76, n = 56 | r = 0.70, n = 54 | r = 0.51, n = 32 | $SO_2$ |
| $H_2S$ | r = 0.52, n = 54 | ------------------ | r = 0.48, n = 73 | r = 0.60, n = 47 | $H_2S$ |
| COS | r = 0.55, n = 75 | r = 0.89, n = 54 | ------------------ | r = 0.75, n = 46 | COS |
| $CS_2$ | r = 0.51, n = 37 | r = 0.74, n = 36 | r = 0.77, n = 37 | ------------------ | $CS_2$ |
| **Paranapiacaba** | $SO_2$ | $H_2S$ | COS | $CS_2$ | |

## *Gas exchange between atmosphere and biosphere*

*Estuary of Rio Cubatão.* Flux measurements of reduced sulphur compounds in the estuaries south of Cubatão were performed at an unvegetated periodically inundated mud flat (Radio Universal). The site has been visited four times in March 1993 to study the exhalation of reduced sulphur compounds under different tidal conditions. Averaged flux and ambient concentration data are contrasted in Figure 10. Ambient concentrations of $H_2S$ display high variability being higher under low tide conditions than during high tide. COS ambient concentrations are elevated and show similar but less pronounced variability compared to $H_2S$ concentrations. $CS_2$ concentrations are low and approximate background levels. Significant contribution from anthropogenic sources may be excluded since all experiments were conducted under sea breeze conditions. Consequently high $H_2S$ concentrations during low tide can be attributed to sulphate reduction in the anoxic sediments of the mud flat. During high tide the evolving $H_2S$ is rapidly oxidized in the water column and partly prevented from entering the atmosphere. The expected high $H_2S$ emission fluxes during low tide have not been observed. On the contrary low tide $H_2S$ emissions are lower than emissions during high tide with maximum fluxes after tidal inundation. This discrepancy may be

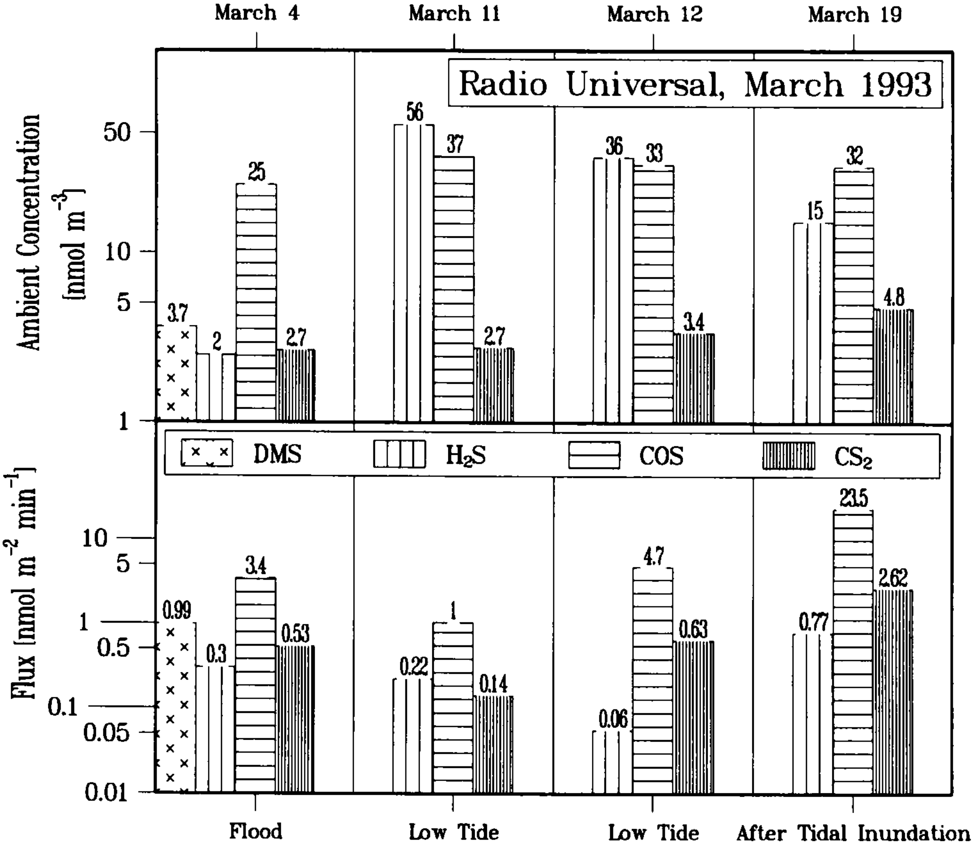

**Figure 10** Fluxes and ambient concentrations of reduced sulphur compounds at the estuary (Radio Universal).

explained by the often observed extreme variability of $H_2S$ emissions in time and space. $H_2S$ emissions are generally in correlation with tidal cycling[2,3]. A large fraction of $H_2S$ is emitted from a narrow region at the water's edge as the tide rises and falls[3]. COS emissions from wetlands have been shown to be positively correlated to solar radiation thus occurring mainly during day-time[2]. At Radio Universal maximum emissions of $H_2S$, COS and $CS_2$ occurred upon tidal inundation which is in good agreement with previous observations. All four experiments were performed during 10:00 and 15:00 local time which might explain the observed high COS fluxes to the atmosphere. The obtained fluxes are in the lower range ($H_2S$), middle range ($CS_2$), and upper range (COS), respectively, compared with data reported on marsh and tidelands in the literature[3,33]. A lack of vegetation at the studied site probably resulted in low DMS emissions which could only be quantified in one case.

*Billings Reservoir.* The investigations of the Billings reservoir on the Atlantic Plateau were mainly dedicated to the anoxic northern part of the freshwater ecosystem. The main branch is strongly anoxic from the pumping station in the north to the bridge of the Imigrantes Motorway in the middle of the reservoir (Figure 11). The anoxic water has a dark green colour and malodorous gas bubbles are rising from the ground. The ambient concentration of $H_2S$ is very high and exceeds the concentration of other compounds by one or two orders

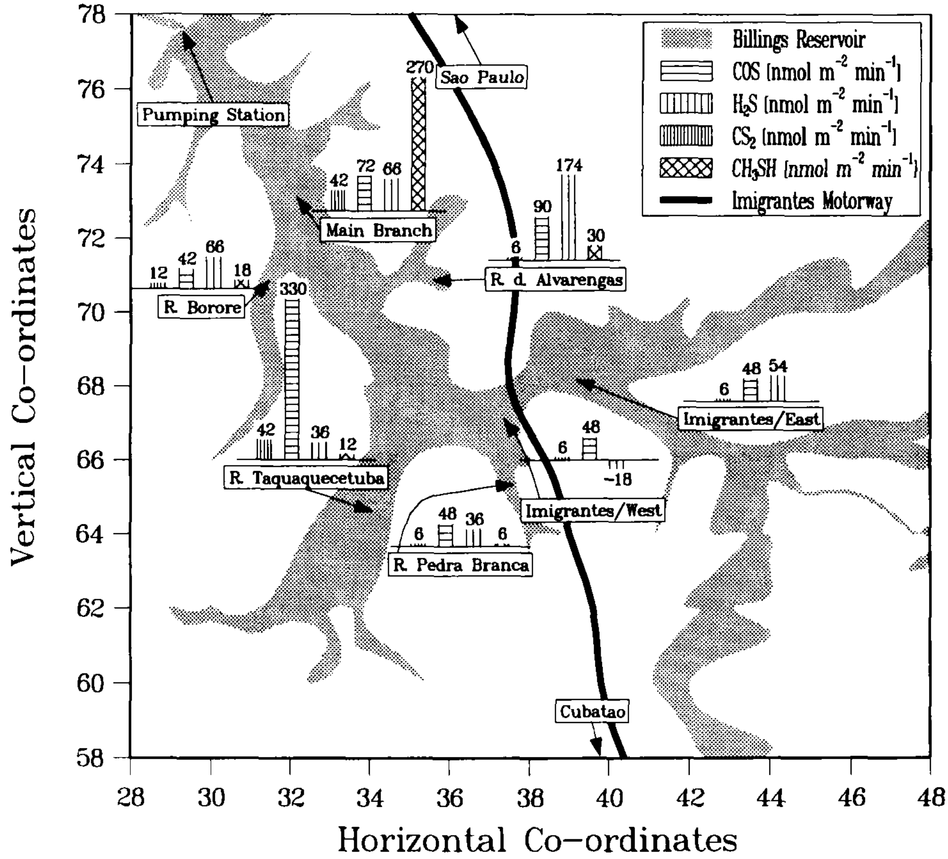

Figure 11 Fluxes of reduced sulphur compounds from the Billings reservoir on September 3, 1992.

of magnitude (Figure 11). Exhalations of $H_2S$, COS, $CS_2$, and $CH_3SH$ could be determined on September 3, 1992 (Figure 12). High fluxes of $CH_3SH$ could only be observed in the most polluted areas. The highest $H_2S$ flux was found near the interface between oxygen free and oxygen containing water in one side branch of the reservoir. All concentrations decrease with increasing distance from the pumping station. Lower concentrations were also found over the side branches of the reservoir. The question whether this strong $H_2S$ source influences the Cubatão area during land breeze has been treated in a previous chapter. The opposite happened during sea breeze on September 14, 1992 (data not shown). On this day ambient concentrations of COS (42–92 nmol$^{-3}$) and $CS_2$ (14–85 nmol m$^{-3}$) were elevated and nearly in the same order as ambient $H_2S$ concentrations. Moreover, maximum COS and $CS_2$ concentrations were observed over an oxic reservoir branch which is located closest to Cubatão. In general low exhalations restricted to DMS are expected from oxic water bodies[10]. A high industrial sulphur burden in the atmosphere should therefore result in deposition of sulphur compounds to the water surface. Deposition fluxes of these compounds to the water surface throughout the reservoir were observed on September 14, 1992 with two exceptions for $H_2S$ in the anoxic part of the reservoir.

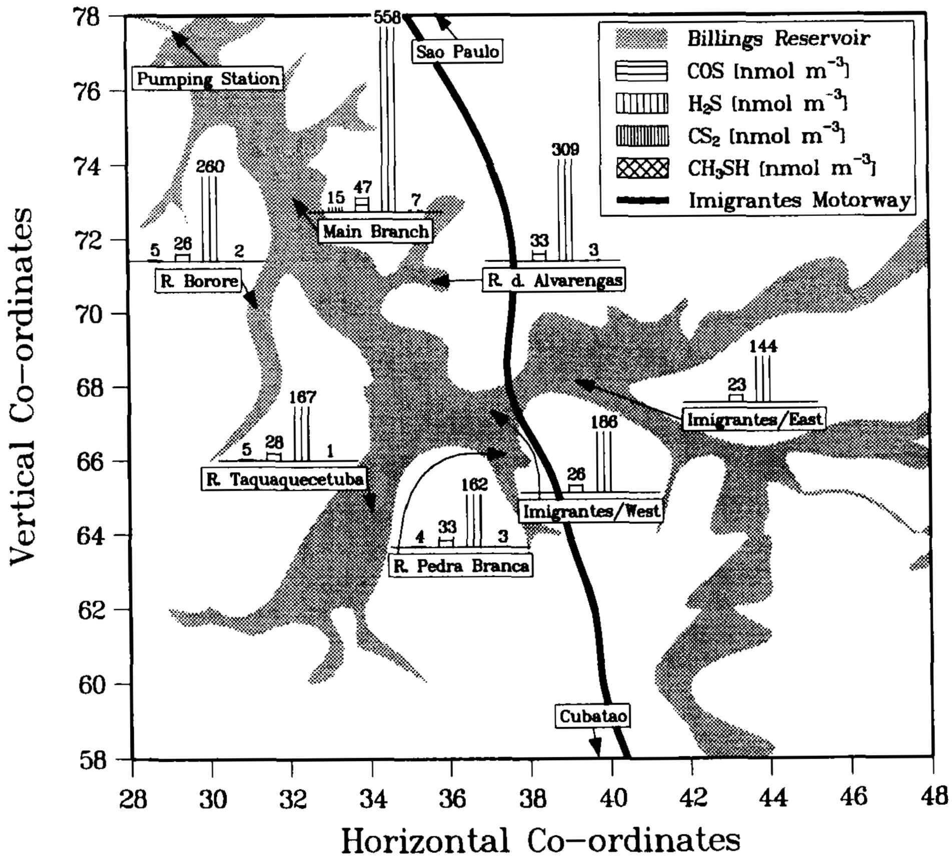

**Figure 12** Ambient concentrations of reduced sulphur compounds at the Billings reservoir on September 3, 1992.

*Vegetated Soils.* Soil and vegetation are the weakest sources of reduced sulphur compounds studied in the Cubatão region. High ambient concentrations and their short-term variability enhance the uncertainty of the calculated fluxes. Due to a considerable residence time of the ambient air inside the flux chamber decreasing ambient concentrations favour measurements of exhalation fluxes and vice versa. Consequently flux data referring to periods of high ambient concentrations have to be interpreted with carefulness. COS, $CS_2$, and $H_2S$ fluxes are concerned. Since DMS and $CH_3SH$ have not been detected in ambient air observed exhalations of these compounds are definite. Some effort has been made to perform flux measurements during land breeze when ambient concentrations are generally low. Nevertheless ambient concentrations of $H_2S$, COS, and $CS_2$ were too high at Paranapiacaba on March 8, at Mogi on March 17, and at Pilões on March 18, too high to yield reliable flux data.

The remaining data are presented in Figure 13. As can be seen exhalation of DMS and $CH_3SH$ could be detected in most of the experiments. Uptake or deposition of $H_2S$ could be

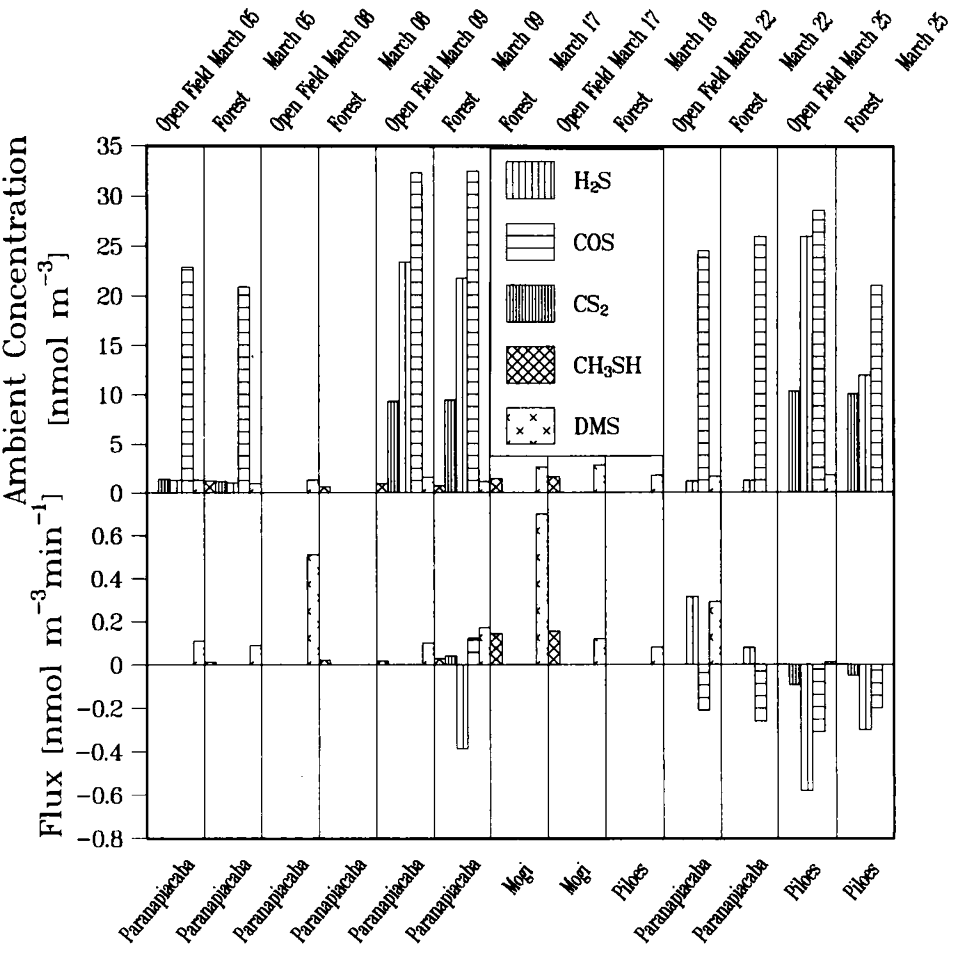

**Figure 13** Ambient concentrations and gas exchange of reduced sulphur compounds between vegetated soils and the atmosphere at three sites of the Serra do Mar.

observed during periods of elevated ambient concentrations of this compound (March 9 and 25). Low ambient concentration levels of $H_2S$ resulted in emission fluxes observed on March 22 at Paranapiacaba both in the open field and in the forest. COS and $CS_2$ show both emission and deposition fluxes with no clear tendency visible. Since all investigated soil plots are vegetated DMS emissions are likely to occur. High DMS emissions have been observed at Paranapiacaba in the open field where the dense vegetation cover consists of grass and herb species. Maximum DMS emissions occurred at Mogi from a broad-leaved herbaceous plant which is common at lower altitudes of the Serra do Mar. The same plant species showed considerably lower DMS exhalations at Pilões. $CH_3SH$ emissions have been observed mainly from forest soils which are covered with leaf litter.

DMS emission fluxes observed in the Serra do Mar can be compared with values published for the Amazon Basin[7,8]. The obtained values for vegetated soils of the Serra do Mar range between values reported for soils covered with leaf litter (wet season: 0.04 nmol $m^{-2}$ $min^{-1}$; dry season: 0.4 nmol $m^{-2}$ $min^{-1}$ and for the forest canopy (wet season: 0.8 nmol $m^{-2}$ $min^{-1}$; dry season: 0.9 nmol $m^{-2}$ $min^{-1}$).

Although little flux data are available until now and emissions depend on various parameters an emission pattern for DMS and $CH_3SH$ with highest exhalations at Mogi and lowest emissions at Pilões can be stated. This hierarchy could be related to the well established pollution gradient between the three sites.

In this context two observations made by the collaborating soil scientists and botanists should be reported. Soil scientists determined sulphate contents in soil water and revealed a sulphate sink between 10 cm and 100 cm soil depth at Paranapiacaba. The sulphate might be either mineralized or taken up by the vegetation. A confirmation of the latter alternative is the elevated sulphur content of plant leaves reported by botanists. An enhanced sulphur emission from living or decaying leaves might be the consequence.

### *Reduced sulphur compounds in surface water*

One river water sample was analysed from the effluent of the hydro-electric generating plant (Usina "Henry Borden") and one from Rio Cubatão (CETESB). One sample has been taken in the estuary (Beira Mar). The three sampling locations are indicated in Figure 14 together with the detected concentrations of reduced sulphur compounds. The two freshwater samples reflect moderate pollution and biological productivity. Generally DMS is the major reduced sulphur compound in oxic freshwater. Concentrations in the range of 0.1–1 nmol $L^{-1}$ have been found in the Great Lakes (U.S.A.) during summer[10]. DMS concentrations found in river water samples of the Cubatão area fit well into this range. $CH_3SH$ and COS concentrations in the same order of magnitude could be an indication for the presence of anoxic sediments and relatively high loads of organic matter.

The water sample from the estuary shows a completely different concentration pattern with DMS concentrations about one order of magnitude higher than COS, $CS_2$, and $CH_3SH$ concentrations. The obtained values especially those of COS are substantially higher than average values reported for coastal waters[34]. Production of $CS_2$ and $CH_3SH$ is likely to occur in the estuarine sediments[34,35] whereas DMS formation is linked to algal growth. COS is

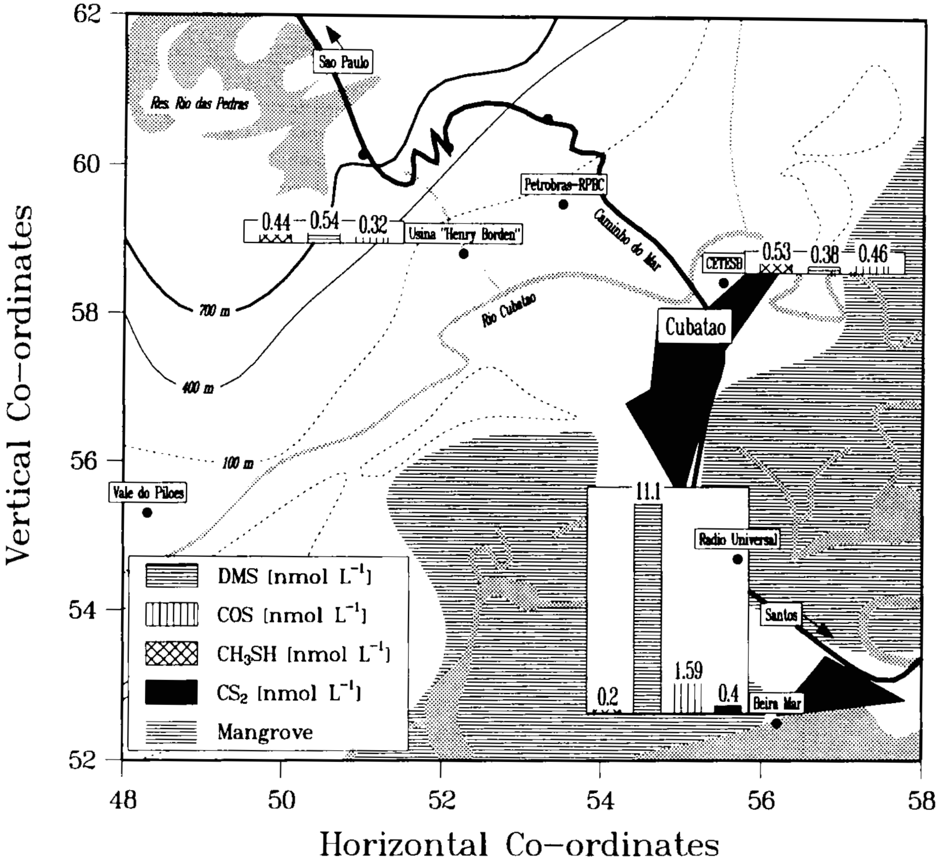

**Figure 14** Concentrations of reduced sulphur compounds in surface water.

known to be photochemically produced in marine surface water in the presence of dissolved organic sulphur compounds[36]. Supersaturation of sea-water with COS leads to considerable exhalation of this compound to the atmosphere especially during day-time. This is in accordance with high COS exhalations measured in the estuary at Radio Universal.

High concentrations of reduced sulphur compounds have been detected in anoxic surface water of the Billings reservoir. Maximum values were: 12 nmol $L^{-1}$ (DMS), 7 nmol $L^{-1}$ ($CH_3SH$), 5 nmol $L^{-1}$ ($CS_2$, and $L^{-1}$ (COS).

## CONCLUSION

In the Cubatão area the presence of high ambient concentrations of $SO_2$, $H_2S$, COS, and $CS_2$ and high wet sulphate deposition has been established with graduated differences between the three measuring stations. Thus the anthropogenic impact on the different ecosystems of the area via the atmosphere has been described. Natural release mechanisms for reduced sulphur compounds have been studied by the aid of an enclosure technique. It has to be emphasized that all results have been obtained with ambient air enclosures. Most of the earlier studies on that subject employed sulphur-free enclosures[3,5,6,36]. Soils within ambient air enclosures act as sources or sinks of reduced sulphur compounds[29]. Sinks turn into sources within sulphur-free enclosures due to a disturbed equilibrium within these enclosures. To consider these effects is extremely important in areas with high ambient sulphur burdens caused by industrial emissions. Since COS is ubiquitous with ambient concentrations mostly above 20 nmol $m^{-3}$ emission fluxes obtained with COS-free air have only limited relevance. These aspects have to be considered when evaluating the flux data obtained in the Serra do Mar region.

Emission fluxes from aquatic ecosystems seem to reflect severe (Billings reservoir) or moderate (estuary) eutrophication which is supported by the respective concentrations of reduced sulphur compounds in surface water.

Fluxes of DMS and $CH_3SH$ from vegetated soils of the Serra do Mar are not significantly different from those reported from unvegetated soils of the Amazon Basin[7,8]. In spite of the paucity of flux measurements performed until now we ascertain a trend towards a positive correlation between DMS and $CH_3SH$ emissions from vegetated soils on the one hand and average ambient $SO_2$ concentrations and wet sulphate deposition on the other hand.

Contrasting of ambient concentration and gas exchange data reveals mutual influences of sulphur sources on each other. Comparison of emission fluxes with ambient concentrations measured at the same site allows a rough judgement whether the chosen site is representative for the studied ecosystem. Discrepancies occurred in the estuary with regard to $H_2S$. We ascribe this to unevenly distributed spot sources in the estuarine sediment with high $H_2S$ emissions leading to high ambient concentrations during low tide whereas the flux from the major part of the area is moderate and lower than the corresponding COS and $CS_2$ fluxes to the atmosphere.

Anthropogenic sulphur sources are clearly dominant in the Cubatão region. In addition emissions of reduced sulphur compounds from eutrophic water bodies and estuarine sediments have to be taken into account for the local sulphur budget. Emissions from vegetated soils are important for single organic sulphur compounds. For the budget of total reduced sulphur these emissions are overcome by deposition or uptake of reduced sulphur compounds of anthropogenic origin.

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