# Performance and results of a six-year German/Brazilian research project in the industrial area of Cubatão/S.P., Brazil

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Abstract: Under the roof of the German-Brazilian Agreement of Cooperation in Scientific Research and Technological Development an interdisciplinary project entitled 'Air Pollution and Vegetation Damage in the Tropics - The Serra do Mar as an Example' was launched in 1989 by Brazilian and German research institutions. During six years investigations were made on transport, transformation and deposition of air pollutants and their effects on soil and vegetation in the coastal mountain range (Serra do Mar) neighbouring the industrial complex of Cubatão/S.P., Brazil. The experimental concepts and the measurements carried out in the field studies as well as the major results obtained are summarized.

#### INTRODUCTION

Air pollution and its effects on ecosystems have been recognized since decades as topical problems around the globe, and accordingly relevant ecological research has been carried out in many parts of the world, in Brazil and Germany as well. Authorities of these two countries concluded that the merging of such efforts in joint bilateral projects should be of advantage for both sides.

For one of the projects specifically the industrial complex of Cubatão, in the State of São Paulo, Brazil, and its immediate neighbourhood in the coastal mountain range, the **Serra do Mar**, were chosen as the investigation area (Fig. 1). Here, favoured by the vicinity of the Santos harbour and the short distance to the most important economic centre of South America, the metropolitan region of São Paulo, 22 large industries developed during 1955 - 1975. These enterprises represent, in terms of air pollution, about 230 emission sources of chemical, siderurgical, petrochemical and fertilizer industrial facilities located in the entrance of the Mogi Valley, where the topographical and meteorological conditions are unfavourable for atmospheric pollution dispersion.

As a result, a strong degradation of the vegetation cover in the Serra do Mar occured between 1962 and 1989 - with slight improvements in some areas after taking mitigation measures in 1985 - favouring a change from well developed primary/secondary forest to low tree and shrub vegetation. Not only the variety of species of this unique evergreen rain forest ecosystem diminished, but also its ecological capacity of maintaining water household and soil stability became disturbed persistently, even affecting physically local industries through land-slides. Due to ongoing efforts of CETESB, the State Agency of Environmental Control, the pollution decreased significantly, but is still far from being acceptable [1]. Therefore it became evident that there was a need for further knowledge on emission, transport, transformation and deposition of air pollutants as a way to understand the complex atmosphere/ecosystem interaction, and also to define actions to reduce the damage caused in the tropical Atlantic Forest in the Serra do Mar. As a response to this task a joint interdisciplinary research program was launched by several Brazilian and German institutions: 'Air Pollution and Vegetation Damage in the Tropics - the Serra do Mar as an Example'

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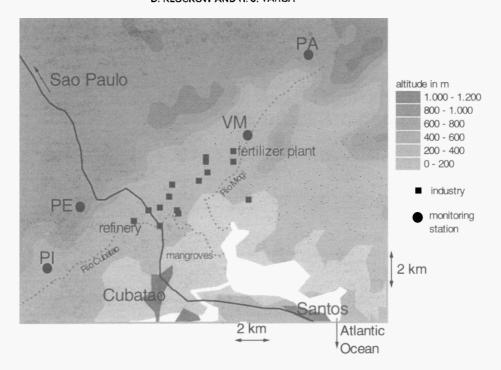


Fig. 1 Investigation area comprising the industrial complex of Cubatão, São Paulo State, Southeastern Brazil. Locations of the major industries at the foot of the Serra do Mar as well as of the monitoring stations are indicated. PI: Piloes (1991 - 1994), PE: Barragem das Pedras (1994 - 1996), VM: Vale do Mogi, PA: Paranapiacaba [2].

#### THE 'SERRA DO MAR' PROJECT

Intensive negotiations between Brazilian and German scientists from 1986 onwards resulted in a joint project definition in 1987 and the signing of a project agreement through GKSS (Forschungszentrum Geesthacht, International Bureau), Germany, and SMA (Secretaria de Estado do Meio Ambiente), São Paulo, Brazil, in 1989. The following overall objectives were layed down:

- 1) To establish a basic knowledge on dispersion, transformation and deposition of air pollutants in and around the industrial area of Cubatão through field experiments and numerical models.
- 2) To provide damage evaluation and risk assessment of vegetation and soil in the Serra do Mar.

The practical work carried out by Brazilian and German scientists started in 1989 and was directed towards achievement of these goals within the framework of 4 work modules, namely 'Atmospheric Circulation and Mass Transport', 'Chemistry', 'Soil', and 'Vegetation'.

From 1991 onwards the project was part of the German / Brazilian tropical ecosystems research program SHIFT (Studies on Human Impact on Forests and Floodplains in the Tropics).

Researchers from the following institutions collaborated on the project:

# - on the Brazilian side

Universidade de São Paulo, Instituto Astronômico e Geofísico (IAG); Companhia de Tecnologia de Saneamento Ambiental - CETESB; Instituto de Botânica - Ibt-SMA; Departamento de Química Analítica, Universidade Federal da Bahia, UFBa; Departamento de Química da Universidade Estadual de Londrina, Paraná;

# - on the German side

Institut für Meteorologie und Klimaforschung, Universität Karlsruhe, Kernforschungszentrum Karlsruhe; Zentrum für Umweltforschung (ZUF), Universität Frankfurt; Fachbereich Landschaftsökologie/Bodenkunde, Universität Kassel; Institut für Angewandte Botanik, Universität Essen; Institut für Experimentalphysik, Freie Universität Berlin Institut für Experimentalphysik und chemische Analytik, Forschungszentrum Geesthacht Institut für Spektrochemie und Angewandte Spektroskopie (ISAS), Dortmund.

The driving force in the running of the project was a common scientific interest in the subjects treated in the different modules, for the Brazilian as well as for the German researchers. Additional motivation came from the fact, that the expected results might help to establish a basis for political decisions towards improvement of the environmental situation in the Cubatão area.

Also in addition

- exchange of scientists between Brazil and Germany
- exchange of know-how and technology
- training and achievement of academic degrees for young Brazilian and German scientists were other important components inherent to the 'Serra do Mar' project [2].

#### THE WORK MODULES

# Atmospheric circulation and mass transport

The Serra do Mar with its steep ascent from sea level up to about 800 m altitude (see Fig. 1) exhibits particularly unfavourable conditions for the dispersion of the pollutants emitted by the industrial activities. Typical meteorological situations are characterized by strong convections, distinct land/sea wind circulations and also stagnating air masses directly in front of the mountain slopes.

Models previously developed for conditions in Central Europe had to be adapted for complex terrains such as those found in the Serra do Mar, in order to simulate and predict wind fields as well as concentration and deposition patterns in the mountain region. The necessary input data - topography, land use, vegetation cover, source strengths, climatological and meteorological parameters - were provided by Brazilian scientists or, for the latter ones, were collected continuously through 3 automatic measuring stations (see Chemistry Module), and additionally, 2 lattices equipped with meteorological instruments.

# Chemistry

The Chemistry Module comprised the measurement of gaseous (e.g. O<sub>3</sub>, SO<sub>2</sub>, NH<sub>3</sub>, HF) and particulate (strong acids and their ammonium salts, heavy metals) compounds, the determination of the composition of rain and cloud water occurring in the Cubatão area, the investigation of scavenging processes and the quantification of wet deposition. It depended to some extent on input from the Circulation and Mass Transport Module and in turn generated the information necessary for the verification of meteorological models and for the assessments made in the Vegetation and Soil Modules.

In order to fulfill these tasks, 3 automatically operating container stations were mounted at different sites (see Fig. 1), frequently in line with the major wind directions. These stations continuously measured the most relevant gaseous pollutants  $(O_3, SO_2, NO_x)$ , as well as meteorological parameters.

In the Chemistry Module special emphasis was placed upon the processes relevant to the composition of rain, cloud and fog water, because the Mogi Valley is an area of generally high humidity with frequent local cloud and fog formation. Therefore, substantial parts of primary and secondary air pollutants are deposited onto the vegetation blanket via the liquid phase. In order to investigate these phenomena, integrating wet only collectors (weekly samples) as well as fractionating rain collectors (for time resolved sampling according to Rain Radar information) were placed at the container station sites. For collection and analysis of the different phases (liquid-gaseous-solid) co-existing in captive clouds, a ground based sampling system was developed and employed. To strengthen the Brazilian/German collaboration, scientists from both countries carried out joint field campaigns in the Cubatão area twice a year. In these periods (each approx. 3 weeks) special investigations were carried out involving compounds such as NH<sub>3</sub>, HF, aldehydes, carboxylic acids, photooxidants, and strong acids and their ammonium salts.

Measurements of the emission of reduced sulfur gases from industry and water reservoirs were also performed.

During one of these campaignes (Oct./Nov. 1994), two LIDAR systems were operated in the study area, with the goal to provide, on an experimental basis, a realistic view on emission fluxes and dispersion of major pollutants (SO<sub>2</sub>, NO<sub>2</sub>, toluene, O<sub>3</sub>, particulate matter) in the complex terrain around Cubatão.

#### Soil

Soil is the final acceptor of most atmospheric substances, natural as well as anthropogenic ones. Therefore, in the Soil Module the effect of the atmospheric input on soil was studied. This included the soil changes induced by atmospheric deposition, transfer of dissolved metals and acids to the groundwater, and changes in the root environment of plants with possible negative effects on vegetation. With this, the Soil Module was closely linked to the Vegetation and the Chemistry Module.

The investigations were carried out at the same sites as the atmospheric and part of the vegetation studies. The methods used included collection of bulk precipitation in the open field and under the vegetation cover on a monthly basis, collection of litter fall under the canopy on a monthly basis, collection of soil water (seepage) at different depths, and measurement of the soil water tension. After determination of major ions and some trace components in the collected material mass fluxes into and through the soil could be derived.

These investigations were completed by laboratory studies on soil samples, e.g. on the adsorption properties with respect to heavy metals or sulfate. One important goal of the investigations was to establish the mass balance for all important chemicals on an annual basis. This balance was expected to give information on the function of the soils as sinks or sources for these substances.

# Vegetation

The Vegetation Module was engaged in investigations on the effects, air pollutants emitted by the industrial complex of Cubatão have on the vegetation of the Atlantic Rain Forest in the Serra do Mar (Mata Atlântica). The aim was to obtain detailed information on type, intensity and causes of vegetation damage. Therefore, the most important phytotoxic components had to be identified by differential diagnosis applying a wide range of techniques from aerial photography to ultrastructural analyses. Basic information with regard to air pollution concentrations and the composition of rain water was provided by the Chemistry Module.

Regularly taken air photographs of the region were used to map vegetation cover and landslides and to detect changes in the degree of vegetation damage. At several sites in the Serra do Mar with different pollution loads, an intensive research program into the effects of air pollution on native tree species was carried out by several work groups. Their activities consisted of chemical analyses of leaf material (changes in nutrient balance and accumulation of toxic elements such as F, S, and heavy metals), investigations on biochemical stress parameters and detoxification mechanisms, measurements of gas exchange and studies on plant anatomy. Phytosociological surveys of tree stratum and herb layer were performed in order to find out to what extent pollution stress had altered the vegetation cover. These methods were expected to provide information on resistance and sensitivity of native species and on the repair and detoxification mechanisms in plants.

Special emphasis was placed on the active monitoring of air pollutants by means of indicator plants. This program aimed at providing data on the spatial and temporal distribution of air pollution effects and at drawing conclusions on the causes of vegetation damage. In order to achieve these objectives, exposure systems for bioindicator plants were installed at 13 sites in the Serra do Mar. At intervals of four weeks, indicator plants sensitive to photochemical oxidants and gaseous fluorides as well as accumulation indicators (S, F, metals) were exposed in the field. The effects were evaluated by the estimation of the symptoms of visible injury and chemical analyses. In addition to the standardized indicators, native indicator species were increasingly introduced in order to establish a tool for monitoring air pollutants in tropical and subtropical regions.

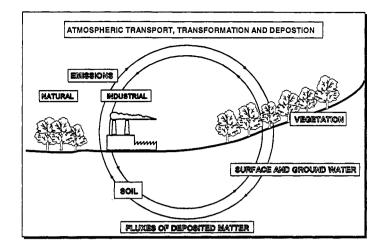


Fig. 2 Concept of the Serra do Mar project [2].

# **MAJOR RESULTS**

Six years of interdisciplinary research on transport, transformation and deposition of air pollutants and their effects on soil and vegetation in the Serra do Mar region have contributed important information to the already existing knowledge on one of the world's most challenging study areas for questions of environmental concern. As shown in Fig. 2, strong emphasis was placed upon estimation of fluxes of emitted matter and its conversion products throug the different environmental compartments, the major target of the project, however, was the 'recipient' Atlantic Rain Forest and its response to man made changes imposed on it.

The most relevant results achieved by the 4 work modules are as follows:

#### Circulation and mass transport [2, 3]

- A sea-breeze occurs which, duing southern summer, passes the coast at 9:30 LST and arrives in the area of São Paulo about 4 hours later, at an average propagation speed of roughly 3 m · s<sup>-1</sup>. The land breeze, from evening to the next morning, is operating at significantly lower speed and leads to mixing of 2 wind regimes.
- Apart from the land-sea-breeze, up- and downslope winds develop at the Serra do Mar; the upslope winds appear at about the same time as the sea-breeze, such supporting the sea-breeze front to overcome the steep slope and penetrate into the municipal area of São Paulo.
- Due to the land-sea-breeze system and the two accompanying south-easterly and north-westerly synoptic wind regimes, deposition of pollutants takes place mainly on the slopes of the Serra do Mar and into the Atlantic Ocean.

#### **Chemistry [2, 4-6]**

- Stack emissions are partly continuous, partly discontinuous
- Frequently 'hot spots' are brought about by the characteristic features of dispersion of the emissions, so that primary and secondary pollutants show maxima up to 4 mg  $NO_2/m^3$ , 3 mg  $SO_2/m^3$ , 0.8 mg toluene/m<sup>3</sup>, 0.2 mg  $O_3/m^3$  in several layers in altitudes between 200 m and 600 m above ground level, here significantly exceeding internationally accepted air quality standards tolerable for vegetation.
- Ground level values hardly ever exceed 20 % of these maximum concentrations.

- The emitted ammonia in the Mogi Valley is of high local influence, in dry as well as in wet deposition; it shifts the pH of rain water in this valley towards neutral to alkaline and leads to high nitrogen input into the ecosystem.
- The spatial distribution of photooxidants (O<sub>3</sub>, PAN) and their precursors as well as of hydrogen fluoride compares well with the respective damages observed on indicator plants.
- For the major ionic species the deposition fluxes through fog and cloud droplet interception is of minor importance when compared with deposition through rain.
- The annual sulfur emission (as SO<sub>2</sub>) from the industrial complex has been estimated to make up 2 % of the total sulfur emissions in Brazil or 1 % of the sulfur emissions in entire South America.

# Soil [2]

- In the Mogi Valley and at Paranapiacaba the exchange complex is almost completely saturated with acids, even in the deeper soil layers.
- Soil internal acid production (HNO<sub>3</sub>) is brought about by mineralization of organic matter and nitrification of deposited ammonia (ammonium), so that in particular at the Mogi site nitrate is released from the soil with seepage such affecting the quality of ground and surface water.
- Through soil acidification significant fractions of the aluminium store are mobilized and becoming available for plant roots in phytotoxic soluble form.
- At the investigated sites the ecosystem exhibits an accelerated nutrient element turnover with loss of nutrients from the soil to the hydrosphere, the situation being particularly alarming with respect to potassium depletion.

# Vegetation [2, 7-12]

- Phytosociological surveys reveal a clear reduction in biodiversity in the Mogi Valley, whereas radial and height growth seem to be more affected at Caminho do Mar (old road connecting Santos and São Paulo, see Fig. 1).
- Forest vegetation from polluted areas shows an accumulation of potentially toxic elements, nutritional imbalances and alterations to wood anatomy that suggest physiological water stress.
- The exposure of bioindicator plants for investigation of effects through differential diagnosis showed ozone-induced leaf damage of sensitve plants over the whole study area, particularly in the middle and higher altitudes, damages through PAN at the Caminho do Mar and at São Paulo, accumulation of sulfur at the Caminho do Mar and in the Mogi Valley and accumulation of fluoride in plants at the Mogi site.
- The observed erosion of the epicuticular wax layer, the mechanical damage through deposited particulate matter and the obstruction of stomata makes plants more susceptible to attack by insects and parasites and may affect photosynthesis.
- The observed reduction of root growth and increase of shoot/root-ratios may affect water economy, mineral nutrition and physical stability of the trees on the steep slopes of the Serra do Mar.
- The present contamination and acidification state of the soils in the study area will habe long-term effects on the vegetation even when emissions are reduced.

# **CONCLUSIONS**

As can be seen from the results presented, the research carried out by the 4 work modules in a discipline oriented but interactive way has made possible the achievement of the aforementioned overall objectives of the project. By this means a basis for decision making has been established which is more sound than it has been before. Proper balancing of ecology and economy, however, will remain the major difficulty for maintaining structure and stability of the unique ecosystem of the Atlantic Rain Forest of the Serra do Mar.

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#### **REFERENCES**

- 1. C.D. Alonso, R. Godinho. Quimica Nova 15, 126-136 (1992)
- D. Klockow, H.J. Targa, W. Vautz (eds.). Air Pollution and Vegetation Damage in the Tropics the Serra do Mar as an Example; final report 1990 - 1996, GKSS, Geesthacht (1997), ISBN 3-00-001579-
- 3. I. Bischoff-Gauß, N. Kalthoff, F. Fiedler. J. Appl. Meteorol. 37, 269-287 (1998)
- 4. W. Jaeschke, J. Dippell, R. Sitals, W. Haunold. In: Sulphur Transformations in Soil Ecosystems (M.J. Hendry, H.R. Krouse, eds.) pp 89-113, Workshop Proc., Saskatoon, Canada, Nov. 5-7, 1992
- 5. W. Jaeschke, J. Dippell, R. Sitals, W. Haunold. Intern. J. Environ. Anal. Chem. 54, 315-337 (1994)
- W. Vautz, M. Schilling, F.L.T. Goncalves, M.C. Solci, O. Massambani, D. Klockow. Water, Air and Soil Pollut. 85, 1973-1978 (1995)
- 7. A. Klumpp, G. Klumpp, M. Domingos. Environ. Pollut. 85, 109-116 (1994)
- 8. G. Klumpp, A. Klumpp, M. Domingos, R. Guderian. Environ. Monitoring and Assessment 35, 27-42 (1995)
- 9. A. Klumpp, G. Klumpp, M. Domingos. Gefahrstoffe Reinhalt. der Luft 56, 27-31 (1996)
- 10. A. Klumpp, G. Klumpp, M. Domingos, M.D. Silva. Water, Air and Soil Pollut. 87, 57-71 (1996)
- 11. A. Klumpp, M. Domingos, G. Klumpp. The Science of the Total Environ. 192, 219-228 (1996)
- 12. A. Klumpp, M. Domingos, R.M. Moraes, G. Klumpp. Chemosphere, in press