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The Po Valley Fog Experiment 1989 What have we learned, where do we go from here?

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ABSTRACT

In this special issue of *Tellus B*, results of the first of a series of joint European field campaigns concerning ground-base cloud experiments (GCE) are reported. The present paper illuminates the background of the experiment before giving answers to the questions of what GCE did achieve in the Po Valley experiment, what lessons have been learned on the way and where ground-based cloud research does go from there.

1. Introduction

As one of the "founding fathers" of the EUROTRAC-subproject for ground-based cloud experiments (GCE), as a member of the Scientific Steering Committee of EUROTRAC and through my close collaboration with the GCE-participants at Stockholm University, I have been involved in the formation and in the realization of the project. These roles have given me a unique perspective of what GCE set out to do and what, in fact, was achieved. To date, two of the three or four planned field campaigns have taken place and the results of the first one directed at radiation fogs in fall 1989 are reported in this special issue of *Tellus B* (Fuzzi et al., 1992). The GCE-group is to be congratulated for their dedicated work leading to substantial achievements in improving our understanding of the physical and chemical processes in fog. As an informed but, I hope, not too biased observer, I would like to give a critical appraisal by addressing the questions what have we learned and where do we go from here?

2. Why did GCE go into the field?

The plan of research for GCE had as starting point instrumental development and individual experiments by the contributing research groups. It was realized at the outset that these individual studies would not be able to encompass the entire multiphase system. Experiments at any one site would not be able to provide the range of system parameters that can be expected in the European region. Accordingly, it was envisioned that joint campaigns were to be conducted at a few sites with widely differing characteristics where the multiphase system was to be studied in detail. The evaluation of those joint campaigns was hoped to relate the differences observed among the sites to the different combinations of controlling factors. Three sites were proposed for study during the first phase of GCE. The first site, Po Valley of Italy, provides fogs characterized by high pollution levels and low supersaturations.

3. Why did GCE go to Po Valley?

One expected a relatively simple multiphase system in the Po Valley radiation fog: a closed system in which a mass-balance approach could be applied to study the internal physical and chemical processes. A detailed description of this system would elucidate the principal physical and chemical processes and most important parameters which control the chemical composition of the fog and the exchange of material among the atmospheric reservoirs of the system.

[1] Contribution no. 688.

4. What did GCE find in Po Valley?

4.1. Meteorology

There were five fog periods during the campaign, but radiation fog at the site was only part of one out of five. The rest were advection fogs, dominated by the advection of either moisture or cold air at the site or advected fogs to the site (Wobrock et al., 1992). No clear role of turbulence in the formation or dissipation of the fogs could be delineated. The dominant processes governing formation and dissipation could not be identified.

4.2. Microphysical characteristics of the fog

There is no report focussing on the microphysical parameters of the fogs. This is surprising because there were dedicated instruments and samplers for the mass and size distribution of the droplets. It has been shown that time series analyses of fog parameters can give new insight into the life cycles of such systems (Welch et al., 1986; Gieray and Wieser, 1992). One can hope that the scattered information which can be found in the present reports will be collected into a systematic microphysical presentation in a future collection of GCE-papers.

4.3. Chemical composition of the multiphase system

The bulk composition of the gas phase and liquid phase reservoirs of the fog did not present a lot surprises. With the exception of the very low SO_2 concentrations, the major species were on concentration levels which had been experienced before in similar multiphase systems (Fuzzi et al., 1992). The phase equilibria and transfer-related properties, on the other hand, yielded interesting results which will be assessed below.

Most of the new sampling and analytical approaches addressed submicrometer particulate matter in and about the fog droplets. The size dependence of the mass concentration of non-volatile material in fog droplets was studied with three complementary methods (Ogren et al., 1992). Two of these were impactors collecting particles on up to eight size stages. The total range covered was ca. 1 to 40 μm droplet diameter. Mass concentrations were found to decrease monotonically with droplet size over the entire observed range. The available information did not allow the investigators to decide which of the possible explanations was the most probable one for this unexpected result. One of the hypotheses considered was the occurrence of growth-retarding material on the surface of the droplets, a possibility that was indicated by several concurrent studies.

Multi-component analyses were performed on droplet residues and on interstitial particle samples. As in most other chemical studies of aerosols, only about 50% of the sampled mass could be explained by the chemical analyses. The scavenged fractions calculated for different species, (Hallberg et al., 1992), as well as multi-variate statistical evaluations of the sample results (Noone et al., 1992a), clearly showed the influence of the chemical composition on the uptake of particles in fog droplets. However, chemical differences could not separated unambiguously from differences in scavenging due to the different size of the various chemical species as evidenced by the measured chemically resolved size distributions (Martinsson et al., 1992b).

A tandem differential mobility analyser (TDMA) was applied to the interstitial and to the out-of-cloud reservoir to study the hygroscopic properties of individual particles (Svenningsson et al., 1992). Two particle populations with different hygroscopic growth were found. These results were shown to have a strong bearing on the nucleation scavenging as determined by other methods.

For the study of fog droplets, two counterflow virtual impactors (CVI) were deployed. Particle size distributions were measured with an internally consistent system of optical counters in the interstitial reservoir and as non-volatile residues in the activated droplets (Noone et al., 1992b). In the Po Valley Fog Experiment 1989, particles below 0.3 μm diameter were not activated, while the scavenged fraction showed a size dependence that indicated an external mixture of particles with different hygroscopic properties, consistent with the other in-situ results and with the results of the particle samples.

4.4. Chemical processes

The system was open as seen from the temporal development of the major S and N species in the different phases (Facchini et al., 1992a). The concept of atmospheric acidity (ACY) and the view of

the chemical processes in terms of titration and back-titration curves proved useful in describing the exchange of basic and acidic components between the different reservoirs of the system. Only negligible production of acidity occurred due to the low concentrations of reactants and oxidants. This fact facilitated the application of the ACY-concept. The results are significantly limited by the fact that exchange processes and chemical reactions in/on non-activated particles could not be studied by the setup of the Po Valley Fog Experiment 1989.

The concentrations of organic compounds were high compared to other experiments (Facchini et al., 1992b). Formaldehyde was by far the most abundant of the three main organic species. While fog represents a sink for soluble organic species, large departures from gas/liquid equilibrium conditions were observed for all species that were investigated. The observed subsaturation in the fog water was most pronounced in the pH region where the equilibria were shifted towards the liquid phase and thus higher mass transport into the droplets was expected. The presence of organic films on the surface of the droplets is not the only but the most likely explanation for the deviations.

4.5. Instrumental development

A number of sampling and measurement systems were either used for the first time or intercompared. Besides a CVI which was designed for chemical sampling, three dedicated methods for measurements of the liquid water content of the fog (LWC), were intercompared (Arends et al., 1992). The forward scattering device PVM-100 clearly proved to be the preferred method for mass-related studies while the PMS-FSSP was necessary for the interpretation of other measurements which were droplet-size dependent.

Two fog water samplers of impactor-type were compared (Schell et al., 1992). Differences in physical (LWC) and chemical (ionic concentrations) results up to $\pm 100\%$ could be reconciled to some extent by applying the available meteorological and microphysical information to the performance characteristics of the instruments. This exercise showed the limited value of such fog water measurements in spatial or temporal cloud profiling, where extensive meteorological and microphysical information is not available at each sampling point.

Aerosol particles were fractionated with respect to their hygroscopic properties and aerodynamic size prior to chemical analyses (Martinsson et al., 1992a). The system supplied valuable information for the understanding of nucleation scavenging in fog as a function of particle size and chemical composition.

5. What have we learned in the Po Valley Fog Experiment 1989?

Earlier, the chemical view of clouds was that of a beaker filled with a mixture of trace gases and a small amount of liquid water, polluted by scavenged particulate matter. The gases were hoped to be in equilibrium with the liquid phase. In particular, when illuminated by the sun a great number of chemical reactions would proceed, the most prominent result of which would be the conversion of sulphur (IV) to sulphur (VI). This oxidation should be fast enough to yield measurable increases in sulphur (VI) after the average lifetime of a cloud.

About 10 years later, clouds were, in a chemical sense, described as flow-through-reactors. A certain range of gas phase and condensed phase reactants enter the reactor in which oxidants lead to the formation of oxidation products. It was recognized that certain physical factors, in particular the evolution of water vapour saturation and the entrainment of outside air can affect the chemical processes in the reactor. The Po Valley Fog Experiment 1989 has shown that even a simple atmospheric system such as a fog would make a rather badly constructed flow-through reactor. In order to understand the flow conditions mesoscale modelling with complex terrain is recommended for future studies.

There were emissions within the system. A significant deposition of fog droplets took place. The atmospheric flow of reactants in and out was beyond the full control of the experimenters. In some of the cases, the fog formation itself took place upstream of the site. Never before was a set of experimental tools as extensive and as sophisticated applied to an atmospheric multiphase system. Nevertheless, we still miss essential processes during the rapid formation of the cloud for lack of time resolution in the chemical measurements. In a highly polluted fog, we cannot

assume mass transfer across phase boundaries to establish equilibrium conditions because of retarding processes at the boundaries. To date, we have no means to assess in situ the processes on the surface of activated or non-activated droplets. We now have to acknowledge that the state of mixing of physical and chemical properties of droplets and interstitial particles varies strongly with their size. Consequently, even the state of the art in size-resolved parametric sampling yielded convoluted results that did not allow clear separations of the effects of particle size from the rest of the particle properties.

6. Where do we go from here?

It will be very hard to overcome the inherent uncertainties in a non-ideal atmospheric system even in a "simple" fog. The micrometeorological coverage can be improved with great efforts approaching those of stand-alone boundary layer meteorological experiments*. In order to study rapid chemical processes during the formation and dissipation of fogs, the time resolution of the chemical sampling needs to improved by an order of magnitude or more. Concerning the condensed phase, single droplet (Bächmann et al., 1992); (Martinsson, personal communication) and single particle analyses (see, e.g., Okada, 1983; Van Dyck et al., 1984; Wieser et al., 1991), appear to be the only solution to the problem of time resolution. While improving the time resolution we must not forget to address "the other 50%" of the condensed phase which is not specified by presently used analytical methods. Since surface properties are expected to be controlling factors, surface analyses in situ are needed. Humidity, measurements of supersaturation on both sides of the 100% level are necessary for the understanding of high resolution chemical measurement in the condensed phase. There is at least one device for direct measurements of this kind (Gerber, 1991).

I know that some of these improvements to the experimental approach have already been implemented in the second GCE-experiment on Kleiner Feldberg, Germany in 1990. More of these will be incorporated in the third experiment on Great Dun Fell, UK in 1993. Thus, I am confident that GCE will continue to provide significant new insights into the physical and chemical processes in the multiphase atmospheric systems over Europe.

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* Within the EUROTRAC project, the planned regional field experiment TRACT = Transport of Air Pollutants over Complex Terrain could be such an exercise.

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