

Local and Regional Ozone: A Student Study Project

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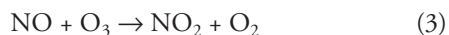
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Tropospheric Ozone Formation and the "Ozone Paradox"

In the troposphere (the lowest 10 km of the atmosphere), ozone is a key indicator of the presence of photochemically active air masses. Ozone has two major sources in the troposphere. One is down-mixing from the stratosphere, where O₃ is formed via photolysis of O₂; the other is photochemical production through a series of reactions from its precursors, nitrogen oxides and volatile organic compounds (VOCs). The latter mechanism may lead to photochemical episodes, which have been observed frequently not only in the USA (e.g., "Los Angeles Smog"), but also in other areas around the globe, including Europe and Asia. Tropospheric ozone formation results from the photolysis of NO₂ by solar light having wavelengths of $\lambda < 400$ nm:

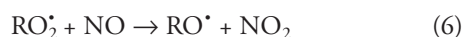


Without NO₂ and its photolysis, there is no tropospheric ozone formation. NO and O₃ react to form NO₂,



A photochemical equilibrium among NO, NO₂, O₃, and the solar radiation is established rapidly; it accounts for higher NO₂/NO ratios at night and lower NO₂/NO ratios during the day. The NO₂ in the lower atmosphere has its origin almost exclusively in reaction 3, and the NO that feeds reaction 3 originates almost exclusively from emissions from combustion sources, such as road traffic. Virtually no NO₂ is directly emitted from these sources. The "paradox" of ozone formation lies in the facts that (i) NO from anthropogenic sources is an essential precursor of regional ozone formation because it produces NO₂, which is photolyzed to produce O₃, and (ii) NO is an important sink of O₃ because it reacts rapidly with atmospheric O₃ (reaction 3). This leads to the situation where the highest O₃ concentrations are normally not observed at the times and locations where the emissions of the precursor, NO, are highest.

The origins of this "paradox" are well understood. As most of the oxides of nitrogen are emitted into the atmosphere as NO, reactions 1–3 will not lead to net formation of O₃. Another mechanism that oxidizes NO to NO₂ without consumption of O₃ is needed. In polluted air masses, the most important pathway is the attack on a VOC by the hydroxyl radical and abstraction of an H atom. The resulting alkyl radicals react with oxygen to form alkyl peroxy radicals which oxidize NO:



Therefore, reactive hydrocarbons are also important precursors of tropospheric ozone. However, the reaction expressed through

eq 4 is slower than reactions 1–3, and NO₂ is formed within minutes and hours through the oxidation by RO₂[•]. In the intervening time, atmospheric transport may lift air masses hundreds of meters or advect them horizontally by up to many kilometers. This contributes to the paradox that the ozone concentrations are often not highest where the emissions of the precursors are highest. Further complications arise from the fact that ozone is almost ubiquitous in the troposphere and any ozone precursors (NO_x, which is NO + NO₂, and VOC) are in most cases emitted into air masses that already contain O₃.

From the lecture hall, these phenomena are well known to students in environmental sciences, meteorology, and atmospheric chemistry (1, 2). However, there seems to be a need to transmit a better understanding of the issues involved, mainly because the chemical processes and the transport processes are often taught in separate courses such as "chemistry" and "meteorology".

The Experimental Plan

Bayreuth is a city with 73,000 inhabitants in the center of Europe (see Fig. 1). It is located about 330 m above sea level in northern Bavaria, Germany, relatively close to the

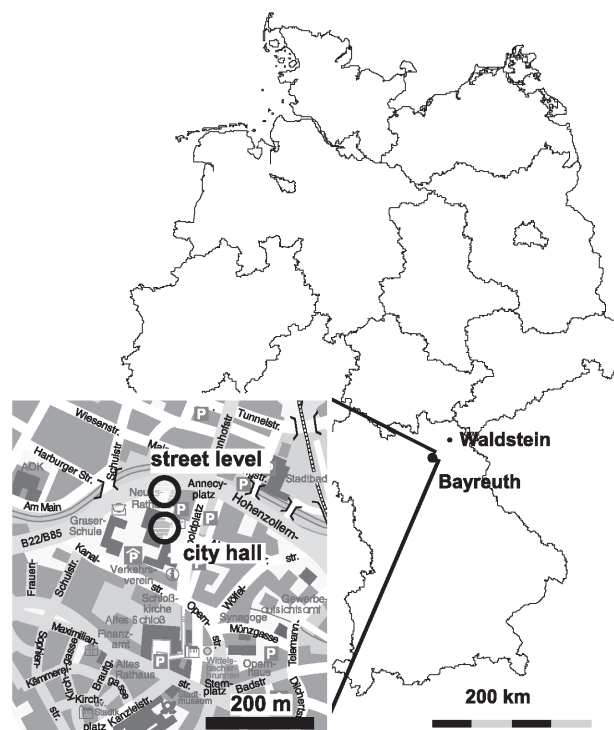


Figure 1. Map of Germany with state boundaries, the city of Bayreuth, and the location of the Waldstein research site. The inset shows a section of the city center, indicating the locations of the field sites "city hall" (13-story building) and "street level". The Eremitage site is in the eastern outskirts of the city.

border with the Czech Republic in the East. It is home to a university and small- and medium-sized industries, as well as a local administration center. It lies in the valley of the Red Main River. Road traffic, which is the dominant source of air pollution, is most dense on a traffic circle (diameter \approx 1 km) surrounding the city center. Close to one of the intersections along the traffic beltway, the state environmental agency (Bayerisches Landesamt für Umweltschutz, LfU) operates an air pollutant observation station. The 13-story city hall, the highest building in the town center, is located about 50 m to the south.

The assignment for the students' study project was to set up an additional air pollutant research station at the top level of the building in order to study the dynamics of ozone and its precursors at the street level and in a vertical column about 53 m high. The station was to be run for about six weeks during the summer of 1999; consequently the chance to catch a period with photochemical smog formation would be high. A second station in the easterly outskirts of the city was set up by the LfU for the same time period, and data from a research station in the Fichtelgebirge mountains about 30 km to the northeast were also available. With the data from these stations, a regional analysis of the patterns of O_3 concentrations was possible.

Besides meteorological parameters such as air temperature, air humidity, and wind direction and speed, the concentrations of O_3 , NO, and NO_2 were measured continuously at most of the stations. The analytical methods employed are well established in air quality monitoring networks in the United States, Europe, and elsewhere, and are described by Finlayson-Pitts and Pitts (*J*). Briefly, O_3 is measured by UV absorption, NO is measured by chemiluminescence with O_3 , and NO_2 is reduced to NO with a molybdenum converter and subsequently measured as NO. For the analysis of the atmospheric concentrations of volatile organic compounds, which are important precursors of O_3 (reactions 4–6), a limited number of canister samples (six) could be taken for further analysis in the laboratory (*3*). The students were given full responsibility for deciding—considering the actual photochemical situation and the weather forecast—when and where these samples were taken.

The Educational Goals

The main purposes of this experiment were to teach atmospheric ozone formation in all its aspects and to instill a deep understanding of the local and regional dynamics of O_3 and its precursors. For instance, principles of chemical kinetics alone do not lead to an understanding of spatial and temporal patterns of air pollutant concentrations in the lower troposphere. Physical phenomena such as transport must also be included.

Other aspects are also very important. The students should learn how an air chemistry field experiment is realized. Important steps are the formulation of hypotheses, the selection of measurement sites, the set-up and operation of the research station, data collection, harmonization and synchronization of various data sets including quality assurance, data presentation, data analysis, and last but not least, the dissemination of information to the public through cooperation with local and regional authorities and the preparation of news-

paper articles. The participating students were in their 3rd or 4th year at the university level (senior undergraduate or graduate) and were encouraged to work responsibly and independently to the maximum extent possible. The formation of working groups and the dissemination of information fell under their own responsibility. They work with real data, and the collection of unique data sets was a strong motivation.

Experimental Results

General

To characterize the concentration of a trace gas in the atmosphere, we use mixing ratios in the unit ppb, which stands for parts per billion (10^{-9}). In atmospheric chemistry, this unit is widely used because the mixing ratio of a trace gas in air does not change when the density of the air changes owing to temperature or pressure changes. Furthermore, mixing ratios characterize the content of a trace gas in air on a mol/mol or volume/volume basis, which facilitates the interpretation of stoichiometric reactions such as reaction 3. In atmospheric chemistry, concentrations (e.g., $\mu\text{g m}^{-3}$) are less straightforward to interpret, particularly because the volume (m^3) sometimes refers to the actual volume and sometimes to a standard volume of air.

Nitrogen Oxides

Our first attention is directed towards the temporal change of the NO_x mixing ratios at the various stations. The middle panel of Figure 2 shows that the highest NO_x mixing ratios were always observed at the street-level station. This result seems to be consistent with the location of the station close to street traffic, which is the major emission source of NO_x . However, the temporal change of the NO_x mixing ratio at this station needs further analysis. We would expect the highest mixing ratios at the times when the traffic is most intense—namely, during the morning and evening rush hours between 06 and 07 h CET in the morning and between 15 and 17 h in the evenings, at least during the work days (Monday through Friday). The mornings show peaks nicely on all days, although their intensity varies. On some days, there are additional very pronounced peaks. Afternoon traffic rush hours appear not to induce these peaks. For example, between Friday and Saturday nights, the highest NO_x mixing ratios occurred around 22 h, more indicative of “party traffic” than any business rush hours during the afternoons.

The lower two panels in Figure 2 show some meteorological parameters and give us clear indications of the causes for the pattern of NO_x in the city center. Very low wind speeds are associated with approximately equal temperatures between the street and the roof levels, in one case even with a temperature inversion (i.e., lower temperature at the street level than at the roof level [night between 04 and 05 July]). During these conditions, the atmosphere stabilizes and vertical and horizontal turbulent exchanges of air masses are limited. This favors the accumulation of primary air pollutants (such as NO_x) in the vicinity of the emission sources at street level. This is the main reason why, despite lower traffic density, the NO_x mixing ratios tend to be higher during the nights at street level.

The station at roof level shows NO_x mixing ratios generally lower than those at street level because the vertical transport

of air masses that are spiked with primary pollutants is always associated with dilution. During daylight hours, the time record of the NO_x mixing ratio is also considerably smoothed compared to the data at street level. During the night, however, a surface inversion layer forms that extends at least up to the roof level (lower panel of Fig. 2). Within this entire layer, the mixing ratios of the primary pollutants (such as NO_x) are strongly enhanced during the nights. Note that in some cases (e.g., during the night from 02 to 03 July), the maximum NO_x is reached about one hour later at roof level than at street level, giving some indication of the vertical travel time for air parcels during stagnant conditions.

An entirely different pattern becomes evident for the Waldstein site. This station, located 780 m above sea level, represents a Central European rural background site. The median NO_x mixing ratio for the period as shown in Figure 2 is 2.4 ppb, and the variability is low. The Eremitage site (see Fig. 1) exhibits a mixed rural/urban character: during extended time periods, the pattern is very similar to that from the Waldstein site (even though the mixing ratios are higher by about a factor of 2); however, on 01 and 02 July, the pattern is similar to that of the city stations. During these two days, the direct influences of the city and the nearby Autobahn become evident.

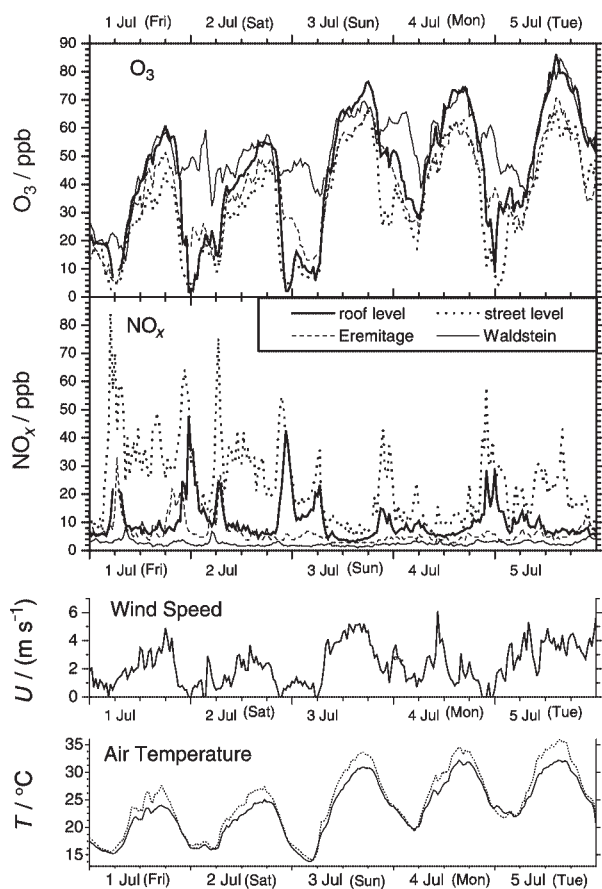


Figure 2. Five-day time series of (top panel) O_3 and (2nd panel) NO_x at the four stations representing various types of sites. The 3rd panel shows the wind speed U (m s^{-1}) at the roof level of the 13-story city hall and the bottom panel shows the air temperature at (solid line) roof and (dotted line) street level.

Ozone

The ozone mixing ratio pattern at each site is more complex than that of NO_x because O_3 is not directly emitted, but is formed in the atmosphere through a mechanism that involves photochemical reactions. Generally speaking, it is expected that O_3 mixing ratios will increase during the daylight hours. In air masses containing large amounts of NO_x , we expect, according to the photochemical equilibrium (eqs 1–3), higher O_3 and NO mixing ratios during the days and correspondingly higher NO_2 mixing ratios during the nights. Figure 2 (top panel) shows the diurnal cycle of O_3 at the station Waldstein, which has an amplitude on the order of 30 ppb or more. Given the low NO_x mixing ratios, below 8 ppb, the cycling of NO and NO_2 cannot be the only cause for these large ozone variations. The depletion of boundary layer air is due to gas-phase deposition of ozone on the vegetation. Dry deposition to any type of surface is an efficient process for removal of O_3 from the atmosphere.

The diurnal cycle of the O_3 mixing ratio is more pronounced at the city stations than at the remote site. Certainly, dry deposition also plays a role here. However, additional effects come into play. Ozone is rapidly depleted in the presence of NO from street traffic sources (reaction 3). Therefore, the nightly minima of O_3 at street level approach low values—in some of the nights almost “zero” (Fig. 2). In the mornings, when the night’s inversion breaks up and wind speed increases (i.e., atmospheric turbulence induced by the solar radiation picks up), O_3 is mixed down from a reservoir layer in the atmosphere and reaches the ground level. The depth of this reservoir layer cannot be deduced from our measurements alone but it is likely to extend several hundreds of meters. This mixing process leads to a dilution of NO_x at street level as we observed it earlier (Fig. 2) and to a simultaneous large increase of O_3 . This increase has, of course, nothing to do with the kinetics of atmospheric O_3 production in the first place, but rather reflects a purely dynamic process. In this context it is exciting to observe the dynamics of O_3 at the roof level. During the days, the maximum observed O_3 mixing ratios are almost identical to those at the remote Waldstein site. The roof-level station perfectly represents the regional O_3 pattern. We saw earlier that the NO_x mixing ratios are, at the same time, low. In other words, the roof-level station represents, as a result of vertical and horizontal transport, completely different air masses than the street level station during the midday hours. During the nights with atmospheric stability, the roof-level station shows a pattern almost identical to that from the street level with very low minima. The nitrogen oxides mix upward and are able to deplete the O_3 in the entire column between the street and the roof levels. The Eremitage station shows, as it did for the nitrogen oxides, characteristics of both an urban and a remote site.

Ozone Formation

Volatile organic compounds (VOCs) play an important role in atmospheric production of O_3 (eqs 4–6). However, routine monitoring of their ambient concentrations was not possible within the scope of this student study project. On the basis of the actual weather forecast (German Weather Service) and the prediction of the O_3 distribution (German Environmental Agency), a group of students selected 02 July for collecting air samples for the analysis of VOCs. Four

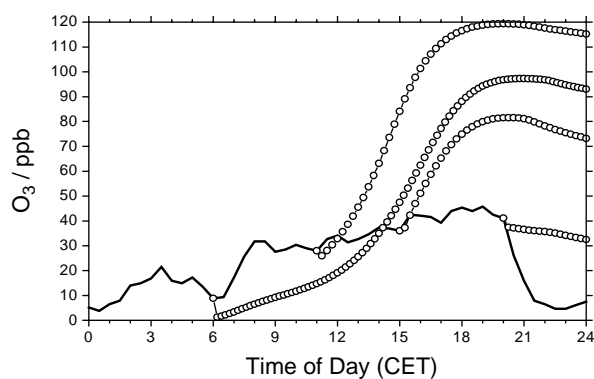


Figure 3. O_3 on 02 July 1999 at the street-level station as measured (solid line) and modeled with a closed-box model, using the VOC sampling times (06, 11, 15, and 20 h) as initial conditions (lines with symbols). The open circles indicate model output in 12–15-min increments. The measured data set is also presented in Figure 2.

samples were collected at the street-level station at 06, 11, 15, and 20 h. The analysis was performed after 3 days by the Fraunhofer Institute for Environmental Atmospheric Research (IFU) in Garmisch-Partenkirchen, Germany, with a GC-FID method described by Habram et al. (3). In total, up to 50 individual VOCs (C2–C9) were quantified in the air samples. Using the Regional Air Chemistry Mechanism (RACM [4]), the measured mixing ratios of VOCs, O_3 , and NO_x , and actual meteorological conditions (temperature, humidity, radiation) as initial parameters, the local production of O_3 was predicted by applying a simple box model (5). As this model predicts only chemical production of O_3 , neglecting all atmospheric transport parameters (dilution/mixing of air masses, deposition to surfaces, etc.), a good agreement between predicted O_3 formation and the measured time series at a station was not necessarily expected. However, a comparison of these two time series is still pedagogically helpful.

Figure 3 shows the time series of O_3 as measured at the street level, together with the O_3 as predicted with the box model, using four different parametrizations as respective start parameters. In all four model output time series, the O_3 mixing ratio drops by a few ppb within the first time step. This reflects an apparent photostationary disequilibrium within the start parameters. This disequilibrium possibly has its origin in the measurement of NO and NO_2 mixing ratios as 30-min averages whereas the VOC samples were taken within about 15 s, so that the respective air masses were not identical. Another possible cause is that the hydroxyl radical (OH), a very important species in atmospheric chemistry, was not included in the initial parameterization of the box model.

After the initial drop, an intense O_3 formation of up to 14 ppb h^{-1} or more was modeled for the air samples taken during the morning and midday hours. This indicated a photochemically very reactive mixture in the air masses at street level. Although a similar increase (14.5 ppb h^{-1}) was also observed between 06 and 07 h at the street-level station, these two effects have not much to do with each other: The former is chemical production as it would take place in a closed box system; the latter is the result of mixing of air masses with low and high O_3 content. The model results show that the air masses, as sampled at street level, exhibit a potential to produce large amounts of O_3 during a day. However, the high

mixing ratios of up to 100 ppb were never reached in the region during July 1999 (c.f. Fig. 2). Dry deposition, mixing, and dilution clearly dampen the potential of these air masses to produce O_3 .

The air sample collected at 20 h showed a slight decrease of O_3 . In the model, this decrease is associated with the consumption of atmospheric OH radicals through reaction with NO_2 . In the absence of photochemistry at night, O_3 is not produced. However, this decrease, again, has little to do with the observed decrease in the measurements. The latter originates from the onset of atmospheric stability associated with low mixing of air masses, which results in an effective depletion of O_3 by reaction with freshly emitted NO.

On a regional scale, deposition to surfaces is another sink process for tropospheric O_3 . The net production of O_3 on a regional scale (production minus losses within the boundary layer of varying depth) can be estimated from the increase of the daily peak mixing ratios at the stations representing the regional O_3 , roof level, and Waldstein. From these data, a net O_3 production rate of approximately 7 ppb per day is derived.

Learning Issues

General

The scope of this student study project offered a series of learning issues, which were covered by student groups with 2–4 members. With the shortage of manpower available to supervise the course, this seemed to be the only possibility to offer participation in the project to a large number of students. However, this was not considered a drawback because advanced students ask for possibilities to work independently to the maximum possible degree. In this section, a selection of a few learning issues is presented in more detail.

Air Sampling for VOC Analysis

The analysis of air samples was performed at an external institute because the required technique was not implemented at the University of Bayreuth at that time. Owing to financial limitations, 6 samples could be taken. The group of students (4 members) had to agree upon a sample plan and define locations and times of samples to be taken. This plan had to be realized utilizing the daily weather and ozone forecasts, which are published in news accounts and the Internet. The supervisor was not at all times fully involved in the planning details. Shortly after completion of the sampling, it was not clear if the sampling times had been selected optimally. However, after completion of the entire experiment and analysis of the entire weather pattern, it turned out that the plan indeed was very close to the best possible option. The students from this group said that the full responsibility (“this is like in real life”) made them learn to study and interpret the weather forecast in a way they had never experienced before.

Raw Data Work

The merging of various data sets from different computers and data loggers, using various operating systems, was a bigger issue than initially anticipated. The transfer of ASCII data files was no problem, but the harmonization of various data formats raised various difficulties. Concentrations and mixing ratios were in different units and there were various formats of time averaging. Although this seems at first not to be a

scientific problem, the complexity of the spreadsheet with more than 2000 rows and 45 columns was quite overwhelming for the students involved in this task. It was surprisingly difficult to maintain control and to produce an error-free data set of quality-assured data. Raw data quality assurance procedures included application of plausibility tests, which are normally best performed by experienced scientists. During this part of the project, close supervision by the senior scientist and intensive discussions about details among the involved students were particularly important and fruitful.

Chemistry versus Transport Kinetics

The kinetics of various important reactions in atmospheric chemistry, such as those outlined in reactions 1–3, are well understood. The second-order rate constant of reaction 3 is $k_3 = 4.5 \times 10^{-4} \text{ ppb}^{-1} \text{ s}^{-1}$. However, for interpretation of data collected in field experiments, these kinetic equations should not always be directly applied without further review. In many cases, turbulent mixing within the atmosphere is not sufficiently intensive to allow for a reaction kinetics, such as the one mentioned above, to be established within a layer of the atmosphere. Such conditions are called “diffusion limitations” of a reaction. In simpler words they mean that two molecules cannot react with each other if they do not find each other. The Damköhler number, together with a description of turbulent mixing within the atmosphere, can be used to estimate the potential of diffusion limitation of a given reaction under given atmospheric conditions. Advanced students appreciate this concept and confirm that such considerations helped them to understand kinetic studies within atmospheric chemistry. See ref 6 for further details.

The Students' Evaluation

After termination of the student study project, an anonymous evaluation sheet was completed and returned by 17 (of a total of 29 participating) students. In addition to answering the questions as given in Table 1, nine students described their point of view in more detail. The selection and wording of questions may have an influence on the results of evaluations.

Table 1. Results of the Evaluation

Question	Av Score ^a
1. Was the topic of the practical course interesting?	4.82
2. Was the scope of the course broad enough so that you could find a topic to develop your special interest?	4.47
3. Were there enough possibilities for you to participate actively?	4.71
4. Was the course well prepared and well supervised?	4.01
5. Did you gain significantly in terms of planning, logistics, and data work?	3.59
6. Did you gain significant knowledge in atmospheric chemistry?	3.76
7. Would you participate again in this course (under a different topic)?	2.53
8. Would you encourage other students to participate in this course?	4.65

^aScoring was on a scale of 1 to 5, with 5 being most favorable. Results are based on the 17 evaluation sheets that were returned.

Analyzing the results presented in Table 1, one should also consider that the practical course in atmospheric chemistry was not obligatory for any of the participants, making it quite likely for high scores to result from the evaluation. Questions 1, 2, 3, and 8 achieved the best scores. This shows that the topic of the course captured the interest of the students and offered them opportunities to work actively. Question 4 returned a surprisingly high score. In the supervisor's opinion, the course was (purposefully) not very well organized logistically, in order to encourage students to become creatively active. One student said the experiments should have been prepared much better in advance; but on the other hand, another said it was a very good feature of the course that the students had to develop their work plans independently. Fifteen students gave questions 5 and 6 scores that were very close to each other (differences 0 and 1, respectively). This was somewhat surprising to the supervisor because the plan was to teach the students aspects of planning, logistics, and data work (question 5). It was assumed that atmospheric chemistry theory would be well understood by the students before start of this course. Only one student fulfilled this preconception, by scoring question 5 with a “4” and question 6 with a “2”. One student even scored question 6 with a “5” points and question 5 with only a “1”, which seems to be an awkward result for a practical course. However, the surprisingly high correlation of the scores to questions 5 and 6 for individual students shows that true understanding of textbook knowledge and practical, hands-on work in the experimental field are closely correlated. This strong positive feedback confirms the necessity of such courses in addition to lecture hall sessions.

Three students said there were too many students (or working groups) actually working in the field and too few doing the actual data work. This is a yet-unresolved problem. Most students want to work with the instruments and data acquisition computers because they believe that they learn most from that type of action. In the early phases of the course, the need and value (including the educational value) of the data work is not recognized by the students and it is therefore difficult to build strong groups for the data work, which includes raw data handling, quality control, merging of various data sets, statistical analyses, presentation in graphical formats, interpretation from various points of views. Toward the end of the course, the few people responsible for data work are overloaded and have trouble completing the tasks, which turned out to be very work-intensive. Toward the end of the course, many of the other students had finished their part and were not able or willing to invest significant amounts of additional time in data analysis. Although anticipating this problem, the supervisor was not able to find a solution agreeable to the students. The field work must be a part of the practical training, and it would probably not be very good to build strong groups for data work at the expense of the field activities for individual students. The time needed for high quality data work is very large and hard to handle for a complicated matter such as regional ozone formation.

Other aspects of the course were mentioned in the evaluation sheets, including the interaction with the Bavarian State Ministry for State Development and Environmental Affairs, which is responsible for regional air quality surveillance. The students visited an operational center and calibration labo-

ratory of this agency. The interaction with the local newspaper (see following section) was also mentioned very positively by a few students.

The relatively low score of question 7 (Table 1) results simply from the fact that some students were about to finish their university studies or had academic interests other than atmospheric chemistry. Overall, the high score of question 8 confirms that this practical course was successful from a pedagogical point of view.

Local Press Response

Topics about air pollution and air chemistry easily trigger public attention. During the summer months, photochemical episodes are always reported in local, regional, and national news accounts. Students participating in this practical course organized an extensive interview with the newspaper of the city of Bayreuth, *Nordbayerischer Kurier*, which appeared as a full page on 01 June 1999. In this interview, the issue of tropospheric ozone production and the ozone paradox was explained to an interested public. After completion of the experimental phase, the students were given opportunity to summarize the results of the study project in the same newspaper on 16 August 1999. In about 200 words, they presented the finding that higher ozone mixing ratios were found in the rural and suburban stations than at the traffic intersection, and they tried to explain the processes involved. The summation of complex matter in 200 words for the general public is certainly a difficult task, but it helped the students to further understand the topic themselves. Furthermore, such efforts are greatly appreciated by local authorities, because they are good vehicles to keep environmental issues a topic of public discussion.

Pedagogical Summary

Pedagogically, this student study project was successful. Many students participated, and their responses on the evaluation sheet were positive in many ways. Learning by doing (viz., the direct observation of chemical processes in the atmospheric boundary layer) is an unmatched approach to understanding the interplay between chemical and physical processes in the development of a photochemical episode. Students were able to learn about selecting sites for air-quality monitoring, setting up the instruments, making decisions on the basis of actual weather forecasts, running the station (including retrieval of raw data, data archiving, and quality control), visualizing complex data sets, extracting important information, and exchanging data among working groups. The formation of small groups of 2–4 members who had to responsibly accomplish individual tasks simulated actual working conditions that the students might meet in their future professional environment. In many applications such as the one described here, chemical and transport processes act on the same temporal and spatial scales in the atmosphere, and any profound understanding of either one (e.g., the chemistry) can be developed only with consideration of the other one. The mixing ratio of atmo-

spheric ozone is not a simple linear function of the mixing ratio of ozone's precursors. Therefore, the students developed a profound understanding of the atmospheric O₃ pattern on both local and regional scales.

Certainly, not every student gained knowledge and experience in all these areas to the same extent. There were definite limitations in personnel and instrumentation that kept the size of the course within time and financial limits.

The response of many students that they learned atmospheric chemistry theory and hands-on work to the same extent (questions 5 and 6, Table 1) was not anticipated. On the other hand, this result confirms the initial hypothesis that the field experiment is a good pedagogical approach for transmitting understanding in atmospheric chemistry.

The problem of forming groups with a good balance between field work and data work remains unsolved.

Acknowledgments

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