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VARIABILITY OF TRACE GASES AT THE ALPINE SITE AROSA IN RELATION TO METEOROLOGICAL PROCESSES

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Abstract

Tropospheric ozone is one of most well known environmental problem with global relevance due to its negative impact on the full planetary ecosystem and its relevance for climate. This work reports the results of extended field measurements of ozone (O_3), of total reactive nitrogen (NO_y) and of some important ozone precursors such as nitrogen oxides (NO_x) and carbon monoxide (CO) at the alpine site of Arosa (Switzerland, 2035 m asl). The study represents an effort in increasing the knowledge on behaviour of trace gases in a complex terrain such as the alpine region which only recently has become a hot target of investigation in the field of atmospheric chemistry. The relationships between trace gas concentrations at the receptor site and meteorological processes determining transport of air pollutants from source areas and tropospheric chemistry are investigated.

Measurements showed the strong dependence of concentrations of air pollutants on season, on weather conditions and on transport processes. Measurements highlighted the role of local emissions from the nearby village in influencing the site of investigation. The interpretation of the measurements indicated that Arosa can not be considered as being directly and regularly exposed to the free troposphere.

In winter the highest ozone and the lowest primary pollutants concentration were found for stable high pressure conditions characterised by temperature inversion. In contrast occurrence of advective weather associated with a more efficient vertical air transport was responsible for the lowest ozone and the highest primary pollutant concentrations. Temperature inversion and advective weather provided an explanation for the positive correlation for ozone and temperature differences between Arosa and Chur. Shifting between such different weather situations was found to strongly influence the lower troposphere up to an altitude of 3500 m asl.

In summer the influence of high pressure situation leads to the highest ozone and NO_y concentration in this season. Measurements during summer fair weather days indicated that trace gases followed a distinctly different behaviour in Arosa as compared to Jungfraujoch (3580 m asl). In Arosa maximal ozone concentrations normally occurred after sunset together with high remaining CO and NO_y concentrations which indicated advection of photochemically well processed air originating from the boundary layer. This result was in clear contrast with the decrease of CO and NO_y concentrations found at Jungfraujoch at night time. This station was much more regularly exposed to free tropospheric air than the site in Arosa.

South foehn transporting air from the Po basin was found to descend in the Arosa basin while crossing the Alps. In spring and summer south foehn events were associated with enhanced ozone concentrations in Arosa. Correlations between ozone and NO_y provided evidence for a recent photochemical origin of ozone during these events. This was further supported by the comparison of ozone concentrations between Arosa and Mt. Cimone (2165 m asl) demonstrating that an ozone accumulation takes place in air parcels moving towards Arosa during the warm season. The negative difference in ozone between both locations during south foehn in the cold season suggested instead that dilution with ozone-poor boundary layer air originating from the Po basin can occur.

In order to investigate the emission-receptor relation on a large European scale air parcels residence over Europe were calculated from backward trajectories ending in Arosa and were linked to ozone measurements. The analysis yielded a weak correlation between ozone concentration in Arosa and air parcels residence time over Europe in the summer months. A generally positive trend between these two quantities was found from March to September when measurements were categorised into different residence time classes. The correlation was not completely appropriate to estimate the hemispheric background because low ozone concentrations in Arosa were often influenced by a frontal passage. The residence time as an estimate for the contact time of air parcels with European pollutant emissions could not account for different specific factors such as weather conditions and differently polluted areas within the continent. However these turned out to be important for photochemical ozone production. For south foehn events no dependence was found between ozone and air parcel residence time over Europe which emphasised once again the strong influence of the Po basin for ozone at Arosa. The long history of an air parcel was found to be more relevant with respect to ozone in Arosa when the analysis was restricted to fair weather days, mostly days with anticyclonic weather conditions. For this purpose the surface solar radiation from ECMWF fields proved to be a qualitatively good tool to separate days with clear sky from days with high degree of sky coverage. The residence time analysis limited to days with fair weather along the trajectories yielded a hemispheric ozone background of about 51 ± 3 ppb for the summer months June and July in accordance with other studies. In this analysis NO_y was used as a measure of NO_x emissions throughout the period of photochemical activity and suggested that pollutant emissions on a regional-continental scale and solar radiation along the trajectories are important factors for the understanding of (high) ozone concentration in Arosa during summer.

Riassunto

L' ozono troposferico rappresenta oggi un problema ambientale globale con possibili conseguenze su tutto l' ecosistema. Questo lavoro presenta i risultati di una campagna di misurazioni svolta ad Arosa (Svizzera, 2035 m) e comprendente misurazioni al suolo di ozono e dei suoi precursori. Questo studio si pone l' obiettivo di migliorare le conoscenze del comportamento di tali gas in un terreno topograficamente complesso come la regione alpina. La ricerca scientifica solo recentemente ha riconosciuto l' importanza di questo tema. Oggetto di studio sono soprattutto le relazioni tra le concentrazioni di tali gas ed i processi meteorologici.

Le misurazioni hanno mostrato la generale dipendenza delle concentrazioni degli inquinanti da fattori come le stagioni, le condizioni meteorologiche ed i vari meccanismi di trasporto ed hanno evidenziato la presenza di emissioni locali. In generale le misurazioni hanno mostrato che la stazione di Arosa non può essere considerata come influenzata direttamente e regolarmente dalla troposfera libera.

In inverno concentrazioni alte d' ozono e concentrationi basse di inquinanti primari sono state misurate durante situazioni di alta pressione associate a inversioni termiche. Concentrazioni basse d' ozono e concentrationi alte di inquinanti primari sono invece state osservate durante situazioni di avvezione caratterizzate generalmente anche da un trasporto d' aria verticale più efficiente. Queste due situazioni meteorologiche sono anche alla base della correlazione positiva calcolata tra le differenze di ozono e di temperatura determinata tra le due stazioni di Arosa e Coira. L' alternanza di queste due situazioni meteorologiche può chiaramente influire la troposfera sino ad un' altezza di 3500 m.

In estate l' influsso di sistemi d' alta pressione si riflette nelle più alte concentrazioni di ozono e di NO_y registrate in questa stagione. Durante giorni contraddistinti da "bel tempo" il comportamento degli inquinanti si é dimostrato essere completamente diverso alle 2 stazioni Arosa e Jungfraujoch (3580 m). Ad Arosa i massimi d' ozono sono generalmente raggiunti dopo il tramonto. Parallelamente le alte concentrazioni di CO e NO_y di notte dimostrano come la stazione rimanga sotto l' influsso di avvezione d'aria caratterizzata da un alto grado d' ossidazione e originaria dallo strato limite planetario. Questo risultato é chiaramente in contrasto con la diminuzione delle concentrazioni di CO e NO_y osservate di notte alla stazione alpina Jungfraujoch, probabilmente più frequentemente esposta all' influsso della troposfera libera.

Il favonio da sud, in grado di trasportare masse d'aria provenienti dalla regione situata sopra il bacino del Po, riesce chiaramente a scendere ad Arosa durante il passaggio delle alpi. In primavera ed in estate periodi di favonio hanno potuto essere associati con alte concentrazioni d' ozono. Correlazioni tra ozono e NOy hanno indicato l' origine fotochimica recente di questo ozono. Un' ulteriore dimostrazione dell' accumulo di ozono in masse d' aria che attraversano il bacino del Po é fornita dal paragone fra le concentrazioni d' ozono misurate ad Arosa con le concentrazioni registrate alla stazione Mte. Cimone (2165 m). La differenza negativa calcolata tra le due stazioni per periodi di favonio limitati alla stagione fredda indica il possibile effetto di diluzione con aria povera d' ozono proveniente dallo strato limite planetario situato sopra area del bacino del Po.

Allo scopo di generalizzare la relazione tra emissioni e ricettore sono stati calcolati i tempi di residenza delle masse d' arie sopra il continente europeo con l' aiuto di traiettorie a ritroso. Tali tempi di residenza sono poi stati paragonati con le concentrazioni d' ozono misurate ad Arosa. L' analisi ha fornito una debole correlazione tra le due quantità durante il periodo estivo. La correlazione tra marzo e settembre diventa più significativa con l' introduzione di classi di tempi di residenza. Tuttavia questa correlazione non é completamente adatta per stimare il "background" emisferico d' ozono. Infatti le basse concentrazioni d' ozono ad Arosa sono state spesso influenzate dal passaggio di sistemi frontali. La quantità "tempi di residenza" chiaramente non riesce a considerare fattori quali le condizioni meteorologiche ed il diverso grado di inquinamento delle varie regioni del continente. Tuttavia queste grandezze sono risultati importanti per la produzione di ozono. Durante periodi di favonio da sud la correlazione tra la concentrazione d' ozono e i tempi di residenza é inesistente, ciò sottolinea ulteriormente l' influsso esercitato dal bacino del Po sulle concentrazioni d' ozono ad Arosa. La storia passata delle masse d' arie relativa al livello d' ozono ad Arosa é risulata essere più rilevante quando l' analisi é stata ristretta a giorni caratterizzati da "bel tempo", in genere giorni caratterizzati dall' influsso di anticicloni. A tale scopo l' utilizzo di dati ECMWF riguardanti la radiazione solare totale ha permesso di separare giorni con maggiore esposizione solare lungo le traiettorie da giorni con alto grado di copertura del cielo. Quest' ultima analisi ha poi usato le concentrazioni NO_y come misura delle emissioni di NO_x lungo le traiettorie. I risultati indicano che le emissioni di precursori su scala regionale-continentale e le condizioni di radiazione solare lungo le traiettorie sono fattori importanti per capire le (alte) concentrazioni estive d' ozono ad Arosa.

1 Introduction

Ozone (O_3) has become nowadays a topic that is also well known and discussed in the public due to its involvement in globally relevant environmental problems. Ozone plays indeed multiple roles in the atmosphere of the earth and can therefore be considered among the most important trace gases (Staehelin *et al.*, 2001). Ozone destruction in the stratosphere (about 10 to 50 km above sea level) by anthropogenically emitted pollutants such as chlorofluorocarbons (CFCs) lead to the ozone hole and was immediately recognised to represent a major problem as stratospheric ozone strongly absorbs solar light in the range 200-300 nm preventing therefore that biologically damaging ultraviolet radiation reach the earth's surface.

At much lower altitudes, in the boundary layer (from the surface up to 2 km), episodes with enhanced ozone concentration are one of the most important environmental and hygienic problem for metropolitan areas and their surroundings since ozone is known to produce adverse affects on human health (Lippmann, 1993). Furthermore ozone also affects rural areas and causes important crop damages in agriculture lowering the plants productivity. Many studies agree that a 25% reduction in ambient ozone would provide benefits of at least $1-2 billion annually only in the United States (Murphy *et al.* 1999). The first indications for photosmog episodes were found already in the 1950s in the Los Angeles basin during stagnant high pressure systems. Today an extensive theory describing the chemical reactions involved in the formation of ozone and of other secondary pollutants in the lower troposphere exists and is referred to as photochemical ozone production (Jenkin and Clemitshaw 2000; Staehelin *et al.* 2000). Enhanced ozone concentrations can be the result of complex conversion of various ozone precursors under influence of sunlight. These include anthropogenically emitted pollutants such as nitrogen oxides (NO_x) and volatile organic compounds (VOC).

The largest ozone concentrations are typically found in the plumes of cities (Thielmann, 2000). The influence of anthropogenic emissions on ozone production is however not restricted to the surrounding of cities. Ozone and its precursors can be indeed transported from source areas towards less polluted sites influencing the ozone budget of these areas (Sillman *et al.* 1990; Wanner *et al.* 1993). The transport of ozone to emission-poor areas was implicitly confirmed by Staehelin *et al.* (1994) that found an over 1-fold increase in ozone concentration between the 1950s and the 1980s by comparing historical measurements at the alpine site Arosa. This increase was found to be consistent with the strong increase of emissions during these 3 decades (Pacyna *et al.* 1991). More recently studies revealed a positive trend in ozone in the low troposphere over years and indicated that such an increase was not only a local or regional phenomenon but rather a hemispheric scale phenomenon (see studies cited in Broennimann *et al.* 2002).

A serious of measure aiming to the reduction of ozone precursors were undertaken in Switzerland since the second half of the 1980s and were followed during the 1990s by similar regulation policies in many European countries (BUWAL, 1997). The success of these emissions restrictions was however not accompanied by any general decrease in ozone concentration (Kuebler *et al.* 2001). By analysing the ozone trend in the 1990s at several locations in Switzerland Broennimann *et al.* (2002) found changes in the frequency distribution of ozone levels leading to a decrease of maximal peaks but also to a significant increase in the ozone mean.

This trend could be only partially explained by the reduction in ozone precursors and the complex chemistry that they undergo. Naja *et al.* (2002) suggested that the lack of ozone decrease could also be the result of a large increase in Asian ozone precursor emissions such as NO_x (Figure 1).

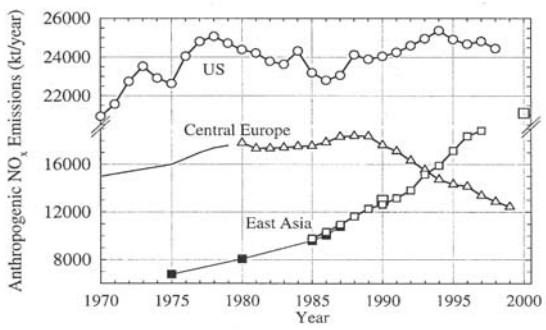


Figure 1: Progressive changes in anthropogenic NO_x emissions over US, Central Europe and East Asia (Naja *et al.*, 2002)

Ozone produced in the boundary layer can reach high altitudes in the free troposphere (Beck *et al.* 1997) from where it can be transported over long distances (Schmitt and Carretero 1997) even on a intercontinental scale (Jaffe *et al.* 1999; Huntrieser *et al.*, 2002; Li *et al.* 2002). Ozone transport is especially efficient in the upper troposphere because at this location the life time of ozone increases from hours to days even reaching several weeks. This is due to the lack of relevant chemical or physical ozone loss processes (Crutzen 1995). The ozone increase in the free troposphere has also important implications for the climate because ozone acts as an efficient greenhouse gas. It is especially in the upper troposphere that ozone contributes to the significantly radiative forcing (IPPC 1996).

High alpine sites are generally located far away from the direct influence of urban plumes. Due to their altitude they are often more exposed to the synoptic circulation than stations located at lower altitude. At high altitude stations the pollutants concentrations are often determined by transport processes on a regional scale (Forrer *et al.*, 2000; Wotawa *et al.* 2000). It is however only in the recent past that atmospheric chemistry issues have become a topic of specific studies in mountainous areas. Measurements at Jungfraujoch have been used in order to investigate background tendencies of trace gases and photochemical activity in the undisturbed free troposphere (Zanis, 1999). Nevertheless the Alpine region can enhance the vertical transport of pollutants from the boundary layer to the lower free troposphere as it acts as a mechanical obstacle and it intensifies thermally driven transport (Furger *et al.*, 2000; Zellweger *et al.* 2000; Tscherwenka *et al.* 1998) Thus the position of high Alpine sites between the boundary layer and the lower free troposphere offers scientifically challenging features such as boundary layer-free troposphere vertical exchange or “horizontal” transport towards the Alps from more distant location.

This study reports the results of two years set of measurements performed at the alpine site Arosa. Measurements include ozone (O_3), nitrogen oxides (NO_x), total reactive nitrogen (NO_y) and carbon monoxide (CO). The station is especially interesting because there are no other measurement sites at about 2000 m in the Swiss alpine area. These data will be evaluated in connection with the meteorological variability and the transport processes. Chapter 2 will include a brief overview on the

current understanding of ozone formation in the lower troposphere and on the most important transport processes. Chapter 3 will present the investigation site Arosa including the instrumentation, the quality assurance procedures and some important tools for the evaluation. Chapter 4 will contain a condensed summary of the measurement results. Chapters dedicated to the discussion of such measurements will thereon follow. Chapter 5 will present case studies in which trace gas concentrations in Arosa were clearly influenced by synoptic weather. Chapter 6 will discussed the diurnal variation of trace gases in Arosa in the different seasons and will compare Arosa data with measurements performed at lower altitude stations (Taenikon) and at the remote alpine station Jungfraujoch. Chapter 7 will show the results of an evaluation of ozone measurements using backward trajectories ending at the receptor site. A final summary of the results will be treated together with the conclusion in Chapter 8.

2 Theoretical background

This section will present a short overview over the relevant processes which determine the trace gas concentration in the lower troposphere. Section 2.1 will deal with the main chemical reactions steering the photochemical ozone production, based on detailed and comprehensive literature (Jenkin & Clemitshaw, 2000; Staehelin *et al.*, 2000). Section 2.2 will be instead devoted to deposition processes. The last section 2.3 deals with transport processes on different scales with particular focus on the Alpine environment.

2.1 Chemical processes of ozone production

Ozone (O_3) production occurs at day time as result of a combination of photochemical reactions. Ozone in the low troposphere is deriving essentially from nitrogen dioxide (NO_2) photolysis which takes place in a wavelengths band (λ) between 300 and 430 nm (UV) leading first to atomic oxygen, which quickly reacts with molecular oxygen yielding to O_3 (R 1). In a second step NO is rapidly converted back to NO_2 by a reaction with O_3 (R 2). Both reactions lead to a photochemical equilibrium between ozone and NO_x ($NO+NO_2$) in which no net ozone production takes place. This equilibrium is often referred as “photostationary steady state” and ozone concentration at this state can be calculated from the NO_x concentration and the reaction rate J_{NO2} (R 1) and k_2 (R 2).

R 1: $NO_2 + h\nu \xrightarrow{O_2} NO + O_3$

R 2: $NO + O_3 \rightarrow NO_2 + O_2$

In the plumes of polluted areas ozone concentrations are observed which are higher than expected from the photostationary steady state. The reason for this is the oxidation of NO (R 2) by compounds formed during the degradation of volatile hydrocarbons (RH) and/or carbon monoxide (CO). Reactions R 3 to R 7 describe in a simplified form the processes responsible for the deviation from the photostationary state. The oxidation of volatile hydrocarbons is initialised by their reactions with free radicals; key players are OH-radicals. Peroxyradicals and hydroperoxyradicals in reactions R 4 and R 5 are the key reactants responsible for NO oxidation and thus for net ozone production. Reactions R 4 and R 5 reflect NO_x-dependent ozone production.

R 3: $RH + OH \xrightarrow{O_2} RO_2 + H_2O$

R 4: $RO_2 + NO \xrightarrow{O_2} NO_2 + HO_2 + CARB$

R 5: $HO_2 + NO \longrightarrow OH + NO_2$

R 6: $2 * (NO_2 + h\nu \xrightarrow{O_2} NO + O_3)$

R 7: $RH + 4O_2 + h\nu \longrightarrow 2O_3 + CARB + H_2O$

Degradation of RH leads in a first step to carbonyl compounds (CARB, e.g. aldehyde) that might undergo a similar oxidation mechanism as described in reaction R 3 to R 7 until they are completely oxidised to CO_2. The product amount of the initialising reaction R 3 is limited by the availability of OH-radicals which are mainly formed by O_3 photolysis. The required wavelengths for photolysis in reaction R 8 are about near 290 nm; thus the $O(^1D)$ formation strongly varies as changes in the atmospheric pathlenght accompanying variations in latitudes and season occur.

R 8: $$O_3 + h\nu \longrightarrow O\left(^1D\right) + O_2$$

R 9: $$H_2O + O\left(^1D\right) \xrightarrow{M} 2OH$$

Staehelin *et al.* (2000) described the evolution of photochemical processes occurring in air parcels moving away from a strong emission source which lead to a gradually increment of ozone in the air parcel during the downwind transport. An important chemical sink of NO_x during day time is its conversion to nitric acid (HNO_3) via reaction involving OH (R 8).

R 10: $$OH + NO_2 \xrightarrow{M} HNO_3$$

NO_x may also temporarily be removed from the cycle leading to photochemical O_3 production by peroxyacyl nitrates (PANs) formation during the degradation of hydrocarbons (aldehydes) (R 11). Reaction R 11 leads to an equilibrium which is temperature dependent. When temperature rises, NO_x is released and can thus participate again to photochemical O_3 production. PANs are relevant because NO_x might be efficiently transported over long distances from pollutant source areas to rural and remote areas.

R 11: $$RCO_3 + NO_2 \xleftrightarrow{M} PANs$$

Nitrogen emissions occur mainly as NO_x. In the course of photochemical aging of air parcels NO_x is consumed and products are formed that are commonly referred to NO_z (E 1). The sum NO_x + NO_z is usually abbreviated as NO_y. NO_y can act as a measure of NO_x emission throughout the period of photochemical activity (Sillmann et al., 1990).

E 1:
$$NOz = HNO_3 + HONO + PANs + NO_3 + N_2O_5 + \\ + RONO_2 + RONO + NO_3^- + NO_2^- + \ldots$$

This section described the chemistry leading to ozone formation. Through reaction R 2 ozone can be destroyed by a reaction with NO (process termed as titration). This reaction becomes particularly important in the boundary layer at night time and is favoured by fresh emissions availability.

2.2 Pollutants removal: dry and wet deposition

In addition to ozone titration through the chemical reaction R 2 also physical removal processes determine the concentration of ozone and of other species. These processes are categorised in wet and dry deposition. Wet deposition implies that pollutants dissolve in the fog, in the cloud or in rain droplets; the following removal takes place when these droplets touch the earth's surface. Ozone is not removed by

such a mechanism, but some species of NO_y as HNO_3 and NH_3 can efficiently be removed this way (Colett *et al.*, 1993; Munger *et al*. 1996). Dry deposition describes instead the removal at the ground through adsorption and absorption on materials (Grontoft, 2002; Wesely & Hicks, 2000). The removal rate (also called efficiency of dry deposition) is given as a flux of the pollutant from the lower layer of the atmosphere to the ground. Each pollutant has a certain affinity in beeing deposited which is termed as deposition velocity. Ozone can be removed very efficiently by dry deposition (as well as are other species such HNO_3, H_2O_2, NO_2). Ozone dry deposition is more effective in the boundary layer of hilly terrain and valley floor at night compared to low altitude flat and opened terrain (Figure 2) (Broder & Gygax, 1985). This increase in efficiency is linked to the development of a downslope valley wind at night (see also section 2.3.3) and can eventually lead to very low ozone concentration in the valley floor. Air reaching the bottom of the valley is rather poor in O_3 and the upward airflow, which is associated with the downslope motion for reason of continuity, results in a continuous O_3 depletion occurring within the lower part of the boundary layer (Broder & Gygax 1985).

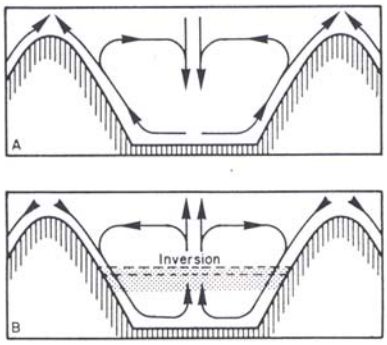


Figure 2: Valley wind system characterized by upslope and up valley wind during the day (A) and downslope and down valley wind at night (B). O_3 destruction due to dry deposition occurs mainly in layers of nocturnal downslope wind where air is transported to the ground during the whole night. Air reaching the bottom of the valley has a very low O_3 content and the upward airflow associated with this local wind system leads to continuous O_3 depletion within the lower part of the boundary layer (Broder & Gygax, 1985).

2.3 Meteorology and transport processes

Photochemical activity and loss processes are basic in understand of ozone and pollutants variability. However, at a site of investigation in the Alps situated far away from pollutants sources, transport processes become important too. A complex terrain such as the Alps is less exposed to fresh emissions than a plain region. At the same time it can however act as a carrier for primary and secondary pollutant which can thus more easily reach higher altitude in the (free) troposphere (Furger *et al.*, 2000). The next sections present some of the mechanism influencing pollutant at an alpine site which are related to known meteorological and transport processes. They are especially valid for ideal situations characterised by a weak synoptic flow (high pressure situation). Deviations from this situation might become strong in cases of, for example, strong advective weather conditions such as during south foehn or a front passage (Forrer *et al.*, 2000).

2.3.1 Inversion and residual layer in summer

This situation refers especially to meteorological processes occurring over opened plain regions (Stull, 1998). These processes are important as they can lead to a fast vertical mixing of pollutants which are transported from the surface up to 1000 – 1500 m above ground (Wanner *et al.*, 1993). From there they can be more exposed to horizontal transport over large distances, e.g towards the Alps (Wotawa *et al.*, 2000).

Thin but stable inversion layers of few hundreds meter develop over the surface at night in summer (Stull, 1998). These nocturnal inversions are rather efficiently separated from the so called residual layer (Figure 3). Pollutants emitted within the inversion layer might accumulate to high concentration whereas layers situated above are protected from the exposure to fresh emissions (Thielmann, 2000). As soon as the sun rises, the nocturnal inversion layer collapses (Stull, 1998). Air over the ground warms faster than air at higher altitude leading to a higher atmospheric instability. In this moment air from the residual layer is mixed down to the surface and air from the surface is transported to higher altitude (entrainment). This leads to a rather homogenously mixed layer that reaches its maximal altitude in the afternoon (Stull, 1998). This provides the most favourable conditions for photochemical activity which causes a strong increase in ozone concentrations in the entire mixed layer (Dommen *et al.*, 1995). A remarkable increase in ozone concentration from morning to afternoon can also occur above the mixed layer (Wanner *et al.*, 1993). At sunset, when air above ground cools down faster than at a higher altitude, the inversion layer is restored over the surface (Stull, 1998). Ozone comparison between the forming residual layer and the previous mixed layer during day time showed a close similarity in concentration (Spirig, 1998).

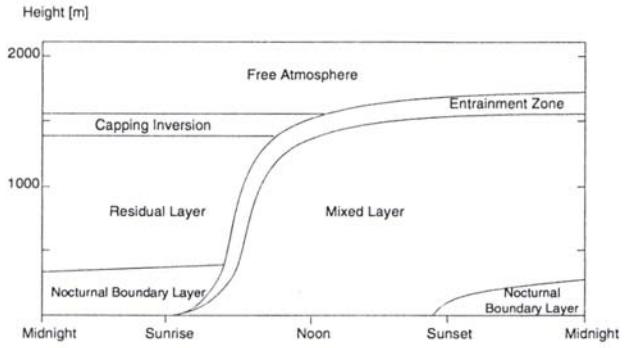


Figure 3: Diurnal development of the boundary layer over opened plain region during a typical summer high pressure situation (Stull, 1998).

During daytime another stable layer arises on top of the mixed layer and acts act as a lid to the rising thermals, thus restraining the domain of turbulence. At night, this capping stable layer can become strong enough to be classified as a temperature inversion. Both layers separate the boundary layer from the free troposphere (Stull, 1998).

2.3.2 Inversion in winter

In late fall and winter very stable inversion layer might develop over the plain region. In contrast to the summer inversion their origin must be regarded as the result of an extensive downward motion of air masses from higher to lower altitude (Häckel, 1993). The adiabatic heating during such motion is accompanied by compression of the air masses which finally might result in paradoxical situation where temperature at higher altitude (e.g. on the mountain) is higher than at lower altitude (e.g. in the plain or valley floor region). These inversions do not dissolve during day time and might last over several days (Häckel, 1993). Strong inversion layers over the polluted plain regions (e.g. the Swiss Plateau) might be relevant for location located below the inversion as pollutants dilution and dispersion processes are inhibited (Dütsch, 1985).

2.3.3 Plain and alpine region interactions and valley wind circulation

During fair weather days in summer the air over the Alps heats faster than over the plain region situated North and South of the Alps. This leads to the development of a local low pressure system over the Alps ("heat low") which induces a general motion of (polluted) air masses from the foreland region toward the Alps during day time. The inflow motion can be strong enough to include an area located 50 – 150 km away from the main alpine valley (Lugauer & Winkler, 2002). After sunset this circulation reverses and air masses flow out from the alpine valley reaching the foreland region, due to more efficient heat loss process over the Alps.

A wind system which induces a vertical transport of air masses develops in the alpine valleys in association with the above described flow pattern. During the day at first upslope winds perpendicular to the valley axis appear followed later by upvalley winds. During the night, downslope and downvalley winds prevail and an inversion is formed on the valley floor (Vergeiner & Dreiseitl, 1987; Whiteman, 1990). This valley wind circulation, or part of it, can occur throughout the year. However it usually shows a seasonal cycle with outflow dominating during the cold season while strong up valley winds reach their highest speed during summer. Variability of the valley wind circulation by the synoptic scale can be of importance. In the Inn valley, for example, the valley wind regime develops mostly during days with weak synoptic flow whereas during strong advective weather types the occurrence of these winds is reduced (Vergeiner & Dreiseitl, 1987).

These wind fields often reflect the measured pollutant concentration. On the valley floor of a pre alpine valley north of the Alps Prevot *et al.* (1993) found strongly reduced O_3 and H_2O_2 concentrations at night time of fair weather days in summer. This reduction was explained by dry deposition and titration with fresh emission occurring below the inversion layer. During the same period but on morning time the same authors found a negative correlation between NO_2 and O_3 on a slope station of the valley. This suggested the motion of air from lower altitude through an upslope wind. The strong increase in H_2O_2 during the afternoon was instead explained by an air mass change in the entire pre alpine valley. The interactions between nocturnal inversion valley wind circulation and synoptic flow were documented in a pre alpine valley south of the Alps by analysing volatile organic compounds and ozone concentration (Prevot *et al.* 2000). At the high alpine station Jungfraujoch Forrer *et al*. (2000) and Zellweger *et al.* (2000) found enhanced values of CO and NO_y concentration during summer and spring time afternoons showing that thermally

driven transport of pollutants from the boundary layer can even reach a station mainly located in the free troposphere.

Recent studies (Furger *et al.* 2000) suggest that in the alpine region, in contrast to flat terrain (see section 2.3.1), in the alpine region there is an additional layer between the (alpine) boundary layer and the free troposphere in summer (Figure 4). This layer originates from the strong upvalley wind circulation which is not closed above the valley but induces a venting of pollutants emitted in the alpine region to higher altitude. This layer might then drift with the synoptic flow across the mountains. For a pre alpine valley it was estimated that within one day the volume of a valley might be flushed up to 5 times in this so called injection layer.

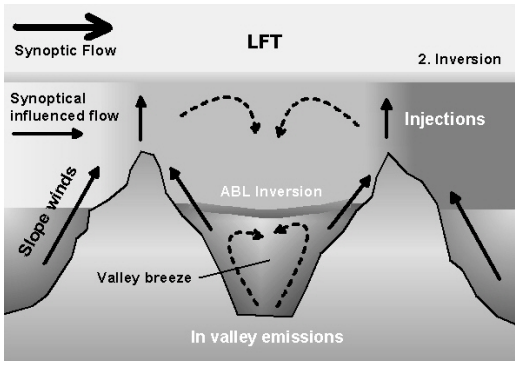


Figure 4: Flow pattern during day time over the Alps during high pressure conditions (summer). Convergent flow is expected in the boundary layer and divergent flow is expected at high altitudes (Lugauer & Winkler, 2002). Typical altitudes of the layers over the core of the Alps in summer: (alpine) boundary layer up to 2000 m (ABL inversion), injection layer between 2000 and 4000 m (injection) and lower free troposphere (LFT from 4000 m (Votalp, 2001). Figure from (Dommen *et al.,* 2002).

2.3.4 Transport towards the Alps and residence time analysis

An air parcel moving over a large area might be exposed to emissions during several days before arriving at a given receptor point in the Alps. This suggests that the long history of the air parcel might have an impact on the pollutants concentrations. This history is often studied by trajectory analysis. A sector analysis based on the origin of backward trajectories has allowed explaining the variation of concentration in NO_y species at the coastal site in Norfolk (Harrison *et al*., 2000). A similar method was also used to assess the influence of regional-scale anthropogenic activity in Northeast Asia on ozone concentration at the remote island Oki in Japan (Pochanart *et al.*, 1999). There were cases in which applying the sector analysis was not successful, for example at Jungfraujoch (Stricker & Staehelin, 1997). One main reason explaining the non applicability of sector analysis in this particular study can be the position of the station in the middle of the polluted European continent. Pochanart *et al.* (2001) instead improved the trajectory analysis by considering the air parcel residence time over Europe (Figure 5). Air parcels transport towards the Alps was termed as residence day over Europe.

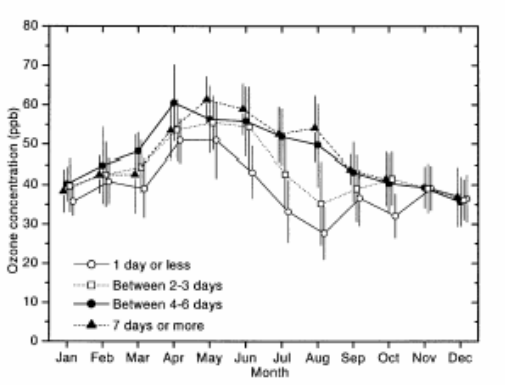


Figure 5: Seasonal variation of O3 in Arosa for air parcels showing different residence time over Europe. Bars indicate the standard deviation within a specific residence time class (Pochanart et al. 2001).

By comparing the ozone concentration in Arosa with residence time of air parcels over Europe Pochanart *et al.* (2001) separated ozone concentrations at the receptor point into distinct residence time classes and postulated that, in summer, accumulation of photochemical produced ozone takes place by increasing air parcel residence time over Europe (Figure 5). This method was applied to the measurement performed within this study.

3 Field measurements and methods

In this chapter an overview is given about the set up of the measurement station and important tools used for the evaluation of the measurements. In addition to a short description of the measurement techniques used in the field campaign, information about quality assurance and data availability is presented at the end of the section dedicated to the instrumentation. In the second part of this chapter the synoptic weather type classification contained in the Alpine Weather Statistics (AWS) and the 3D trajectories are presented

3.1 Measurements in Arosa

3.1.1 Site of field measurements in Arosa

The measurement station is located in the area of Arosa (1850 m) at the end of the Plessur valley, within the east Swiss Alps. The Plessur valley itself is a side valley of the much larger Rhine valley and can be considered a V – shaped valley. The valley is about 25 km long and oriented in a first part from W to E and at the end from N to S-SW (Figure 6). The Arosa basin forms the end of the valley and is surrounded by several mountain peaks reaching 2500 – 3000 m. The valley floor rises from 500 to about 1700 m and the crests overtop the floor in some cases by 1600 m. Except two valleys descending from the Weissfluhjoch area there are not any important side valleys along the Plessur. The measurements evaluated in this work were performed at the site called Tschuggen (2030 m) just above the village of Arosa. The city of Chur located at the entrance of the Plessur valley is with its population of about 40'000 inhabitants and its industrial area the closest centre.

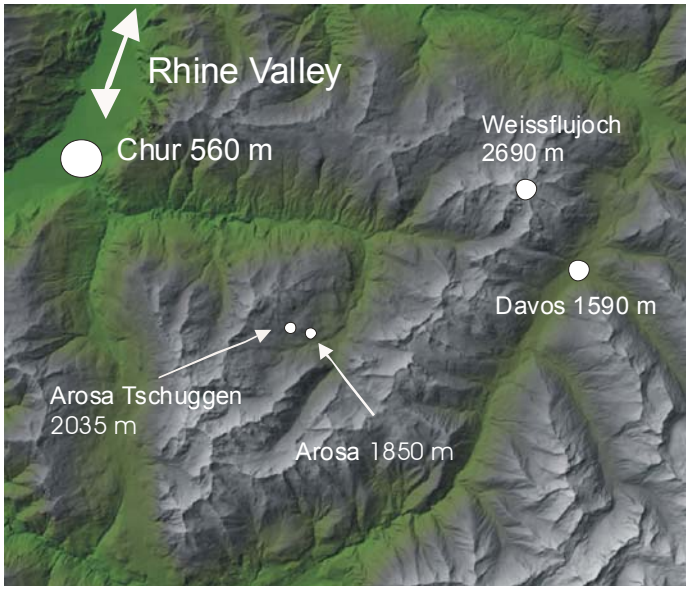


Figure 6: Arosa is located in a mountain region, closed to the Rhine valley (Switzerland, 46.77°N/9.76°E).

Arosa is a popular tourist resort area. The population in that area strongly varies with the season with a peak in winter. While the San Bernardino highway in the Rhine

Valley represents an important north – south route, there is no transit traffic in the Plessur valley itself.

3.1.2 Measurements in Arosa: instrumentation and data quality

3.1.2.1 Overview

The species shown in Table 1 were measured in this work. The same table also includes basic information on the used instruments. In addition to the measured chemical compounds a data set with meteorological measurement performed at the investigation site was available. This dataset includes following parameter: wind direction and wind speed, relative humidity, temperature, global radiation, pressure, and rain fall. Details on these measurements are found by Meteo Swiss (SMA, 1996).

Trace gas	Instrument	Measurement principle	Mess range	Detection limit	Time resolution (mean value)	Calibration Frequency	Number instrument
O_3	O_3 analyzer model 8810 Monitor Labs	UV – absorption	0 – 5 ppm	3 ppb	10 min-1	1 year-1	1
NO	Eco Physics CLD 780 TR	Chemiluminescence	0 – 50 ppb or 0 – 100 ppb	10 ppt	10 min-1	1 d-1	2
NO_2	PLC 760 TECAN	Photolytic converter	-	-	10 min-1	1 d-1	1
NO_y	Intern developed unit	Mo – converter	-	-	10 min-1	1 month –1	1
CO	AL5001 CO monitor Aero laser	VUV fluorescence	0 – 10 ppm	< 2 ppb	10 min-1	2 d-1	1
Calibraion unit				Air pollutants elimination			
	Gas calibrator Environics S100	-	-	-	-	-	1
	Eco physics PAG 002	Oxidation (O_3) + adsorption (charcoal)	-	NO_x and O_3 < 10 ppt	-	-	1

Table 1: Instruments used for trace gas measurements in the field campaign in Arosa. Additional calibration units for nitrogen compounds are listed at the bottom of the Table.

3.1.2.2 Ozone

The instrument employed is a commercially available Monitor Labs instrument (model 8810) which was supplied by the Swiss Federal Laboratories for Materials Testing and Research (courtesy of B. Buchmann, EMPA Dübendorf). This analyser quantifies the UV absorption of ozone in the sampling air (0.8 l/min). A low pressure mercury lamp emits UV light at 253.7 nm which is close to the maximum of the Hartley absorption band of ozone. The instrument alternatively measures ozone in ambient air and air without ozone (reference). In the reference cycle ozone is removed by a scrubber and the intensity of the light of the lamp is measured (I_0). In the second cycle ambient air is directly flushed through the absorption cell. Ozone absorbs the UV light and the remaining light intensity (I) is quantified. The ozone concentration depends on the ratio between I and I_0 and can be calculated by the Beer – Lambert's equation, where ε = the absorption coefficient of ozone at 253.7 nm (m/ppb) and ℓ = the optical path length (m):

E 2: $$[O_3] = \frac{1}{\varepsilon * \ell} * \ln \frac{I_0}{I}$$

The ozone determination can be considered to only depend on the absorption coefficient ε and on the optical path length ℓ.

The ozone analyzer was compared twice with reference instruments. The first time before the measurement campaign the ozone analyzer was calibrated against a NIST Standard Reference Photometer (SRO # 15) at the EMPA (EMPA, 2000). At this time a new ozone scrubber was installed. The second time the ozone analyzer was compared with a TEI 49C – PS (Thermo Enviromental Instrument) applied by the AfU Grabuenden within the regular ring calibration of all the ozone analyzers belonging to the network of the Kanton Graubuenden. The instrument accuracy was determined to be +3 ppb below 120 ppb. The results were used to correct the measured values.

Interferences to a correct O_3 measurement are known to originate from aromatic compounds (Grosjean & Harrison, 1985) and are expected for aerosols. Both influences are expected to be negligible in Arosa. Relative humidity as well is reported to alter the optical characteristics of the windows of the absorption cell (Meyer *et al.,* 1991). This effect (which is not quantified during calibration, as they are performed with dry air) is not believed to be important in the typical measurement range in which we were operating.

3.1.2.3 Nitric oxide and nitrogen dioxide measurement

Measurement of NO and NO_2 were made with a commercially available ECO PHYSICS system which comprises a CLD 780 TR NO analyzer coupled to a Tecan PLC 760 photolytic converter.

A detailed description of the instrument design and on the involved processes can be found in publications of previous projects carried out with this instrument (Brunner, 1998; Jeker, 1999). Here we give only some essential information concerning the coupled NO - NO_2 measurement. The instrument cycles through a sequence of 1) zero air (obtained by exposing the sample air with ozone upstream of the instrument main chamber in order to remove NO) 2) measurement of NO in ambient air, 3) zero air and 4) NO_2 - measurement. Integration- and flushing times were set to last 60 s per cycle. The sampling flow through the instrument was regulated and kept constant to 3 l/min by a critical orifice. The measurement is based on the chemiluminesence of excited NO_2 molecules formed in the reaction of NO with O_3, the relaxation of excited NO_2 - molecules produces a photons flux in a broad band between 600 and 2800 nm that can be detected by a photomultiplier. The O_3 needed is produced from oxygen molecules present in dry air by a silent discharge and added to the sample flow. At room temperature about 6% of the formed NO_2 is present in the excited state and at pressure below 10 mbar about 1% of the excited NO_2 decay to ground state with photoemission. These values seem to be very low, but they are sufficient to measure with high accuracy NO in ambient air, also in very clean air (much less than 1 ppb) (Drummond *et al.*, 1985). In order to prevent too high quenching rate of exited NO_2 with other molecules (mainly O_2, N_2) it is important to keep a low and constant pressure value (< 20 mbar) in the detection chamber of the instrument.

NO_2 in the sample was first converted by a commercially available TECAN PLC 760 photolytic converter and subsequently quantified as NO by the CLD 780 TR NO analyzer. The system uses a 300 W Xenon lamp and operates highly specific for the conversion of NO_2 to NO. The conversion efficiency η decreased monotonically with increasing age of the lamp from about 60% to 25% and regular changes of the lamp were needed. The NO_2 content in the sample was thus calculated by equation E 3, where NO_c is the concentration of converted of NO_2.

E 3:
$$NO_2 = (NO_c - NO) * \frac{1}{\eta}$$

Both CLD 780 TR and the performance of the PLC photolytic converter were calibrated daily. The CLD 780 was calibrated with 9 ppb NO. Using an Environics S100 gas calibrator unit a certified gas mixture of 6 ppm NO in N_2 was diluted with air supplied from an Eco Physics PAG 002 pure air generator. The NO standard used for the determination of the sensitivities was checked after the PIPAPO campaign (Thielmann, 2000). The sensitivity of the CLD 780 TR was constant through the whole campaign and amounted to about 1000 cps/ppb.

Before being installed in Arosa both analyzers were completely cleaned and revised with the help of the supplier company ECO Physics, some parts of the internal sampling tube had to be replaced in order to eliminate leaks. The precision of the CLD 780 TR was determined from the standard deviation during a zero calibration. For the CLD 780 TR the precision was quantified to be 19 ppt. The NO measurement showed sometimes very low values closed to the detection limits of the instrument.

The efficiency of the PLC was measured daily according to a procedure based on gas phase titration of NO with O_3 as described from the USA Environmental Protection Agency (Eco-Physics, 1996). A

large amount of data was lost due to failures of the instrument. Most of this loss has to be attributed to failure of the high voltage power supply and to a smaller extent to failure of the xenon lamp. The fact that this instrument and its original components are no longer commercially available strongly prolonged reparation.

3.1.2.4 Total reactive nitrogen measurement

The compounds belonging to NO_y are converted to NO by a molybdenum (Mo) catalytic converter upstream of a second CLD 780 TR NO. The second CLD 780 instrument only cycled through a sequence of 1) zero air and 2) NO - measurement. Integration - and flushing times were set to last 30 s per cycle; the sampling flow (0.7 l/min) was adapted to the converter by a critical orifice.

The converter was developed in the framework of the PIPAPO project (Thielmann, 2000) and consists of a Mo-mesh (0.04 mm wire diameter, 0.58 mesh width) inserted into a glas cylinder kept at a temperature of about 350 °C by an oven fixed around the converter. The converter was further improved by using a heated teflon inlet covering the previous inlet made from glas according to recommendation of Dommen (PSI, personal comunication). This should enhance the conversion of some NO_y species particularly HNO_3 since it has been shown that any other material than PFA, TFE or FEP Teflon significantly adsorbs HNO_3 (Neumann *et al.*, 1999). In July 2002 a strong lightning destroyed the oven of the converter. For the rest of the campaign (1-2 months) a second converter without a new heated inlet was used.

The sensitivity of the CLD 780 was checked by a daily calibration as for the NO measurement and was during the whole campaign about 300 cps/ppb. The precision of the CLD 780 TR was determined from the standard deviation during a zero calibration. For the TR used for the NO_y measurement the precision was quantified to be 76 ppt.

The efficiency of the NO_y conversion was tested regularly every month with Isopropyl nitrate (IPN). The 4.67 ppm standard was diluted to several ppb levels in the range 1 – 20 ppb by using the gas calibrator unit S100 and the Eco Physics PAG 002 pure air generator. The efficiency of the conversion decreased only slightly during the campaign and was always close to 100% (for IPN). The aim of these tests was to detect possible substantial decrease in the conversion efficiencies. The measurements were not corrected according to these tests. Three times the converter was regenerated during 15 - 20 hours at high temperature (450 - 500 °C) with a constant flow of about 60 ml/min of 7% H_2 in Ar. Because of the melting point of the glass used for our converter we could not heat the converter up to 700 ° C as suggested by Dommen (PSI, personal communication)

The check with IPN is only a simplified test. The NO_y measurement suffers from the fact that not all of the compounds are completely converted. In the framework of the project PIPAPO (Thielmann, 2000) the efficiency of this converter was systematically examined and compared with other converters used at the Paul Scherrer Institute (PSI, Switzerland). The results showed that the conversion is close to the unit for NO_2 and PAN. Nitrates (NO_3-) and HONO are believed to be converted by 40 – 50% under field conditions. For HNO_3 contradictory results were found. From this experience it was suggested to improve the conversion efficiency by a heated Teflon inlet.

3.1.2.5 Carbon monoxide measurement

An AL5001 CO monitor from the company Aero Laser was used to measure carbon monoxide. The basic mechanism of the CO fluorescence is given by reactions R 12 to R 14. Excitation of atmospheric CO occurs by radiation from a CO resonance lamp after having selected the appropriate wavelength interval by means of an optical filter. Besides the fluorescence, the excited CO molecule is also deactivated by collisions with other molecules M, for example N_2 or O_2.

R 12: $CO + h\nu \longrightarrow CO^*$

R 13: $CO^* \longrightarrow CO + h\nu$

R 14: $CO^* + M \longrightarrow CO + M$

The original concept of the instrument dates from the 1980s (Volz & Kley, 1985) and was applied in balloon borne measurements in the stratosphere. The ballon instrument was subsequently adopted and adjusted for measurements aboard a research aircraft (Gerbig *et al.*, 1996). The instrument used in this campaign is mainly based on the optimisation made recently (Gerbig et al., 1999).

The AL5001 consists of one resonance lamp excited by a resonance fluorescence (RF) discharge, an optical filter for selection of the appropriate wavelength interval and a CO fluorescence chamber (Figure 7). The emission of the lamp is collimated within the optical filter to a parallel beam of 150 nm light, using CaF_2 lenses, and then focused into the fluorescence chamber, where the fluorescence from CO is detected at right angles by a photomultiplier with Suprasil preoptics. Two dielectric mirrors in the parallel part of the light beam provide the required spectral band path.
The optical filter is made from aluminum covered with a black coating for reduction of stray light. The operation of the instrument has four different gas flows:

1) The optical filter is completely sealed and gently flushed with ca. 20 ml/min dry N_2 (purity 6.0) which is necessary to avoid absorption of radiation in the Shumann-Runge continuum of molecular oxygen and other impurities, in particular CO. The measurement campaign in Arosa revealed that the high quality of this gas flow is absolutely important. In order to ensure this high level of purity an inert gas purifier from the company *Aeronex* (supplier Winder technologies in Basel) that guarantied a N_2 quality of 9.0 was installed upstream of the instrument after the gas bottle.
2) The resonance lamp is operated with a mixture of CO_2 in Ar at a pressure of 5-7 mbar. The best sensitivity is obtained with a mixture of 0.25% CO_2 in Ar. Contamination of this gas with water can reduce the intensity of the VUV lamp in the wavelength range of 150 nm and therefore it is crucial to use high purity (Ar 6.0).
3) For calibration purpose a third gas flow is needed. A bottle with 1 ppm CO was used directly connected to the instrument.
4) Sample gas flow has to be dried before entering the fluorimeter, as the fluorescence method is also sensitive to water. For this purpose the sample air was circulated at first through an external Nafion tube dryer.

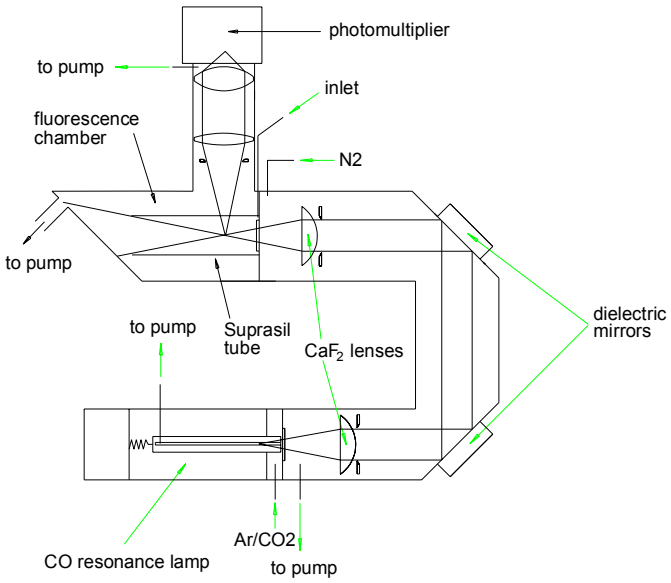


Figure 7: Schematic diagram of the Aero Laser AL5001 CO monitor.

An external pump is used for supplying the sample, the calibration gas or zero air into the fluorescence cell, removing the N_2 and Ar flow and keeping a constant pressure value in the fluorescence cell of 6 to 7 Torr.

Table 2 summarizes the parameter setting used during the campaign. They are the result of several tests and they are supposed to best fit for a measurement at a remote site like in Arosa (for further details about parameter see operating instruction (Aero-laser, 2000)).

The AL5001 at the measurements in Arosa was calibrated every 8 hours (a calibration cycle lasts 4 minutes) with a 1 ppm CO in zero air directly connected to the instrument. The concentrations measured by the instrument were automatically corrected according to the calibration results. The range of the instruments sensitivity is 15 – 55 cps/ppb. Below 10 – 15 cps/ppb maintenance of the

instrument is needed. The decrease down to this lower sensitivity values occurs every 2 – 3 month in case of proper operation of the instrument. All the optical components have to be cleaned every 2 – 3 months (mirrors with ethanol or acetone whereby high purity is necessary, lamp-windows need to be replaced or cleaned with ethanol and aerosol-spray ¼ and 1 μm).

Parameter	Range - Value
Flow lamp	20 – 25 ml/ min
Pressure monochromator	0.9 – 1.3 bar
Pressure cell	6 – 7.5 Torr
Pressure calibration gas	1.2 – 2 bar
Parameter of the counter	T= 1000 ms, A =1
Number of averages for concentration output	30
Number of averages for calibration gas	120

Table 2: Parameter setting of the CO analyzer during measurement in Arosa.

A large amount of data was lost due to failures of the instrument. This loss is attributable to different causes. The analyzer suffered from variation of supplied power that occurred at the measurement station; the installation of one uninterruptible power supply UPS unit it is recommended also for future studies. The quality of the N_2 gas is also important in particular if the instrument continuously measure over a long time. With the installation of the gas purifier much more stable condition was reached. The problem caused by the formation of a deposit of oxidised hydrocarbons on the dielectric mirrors of the monochromator could be removed. As a result the drop in sensitivity within 1 month below the given specification value could be avoided. For long term measurements is also recommended to install a pre filter in the sampling tube in order to avoid dust particles entering the instrument. This was found to be rather important in case of continuous measurement also in Arosa where the ambient air quality is certainly better than other possible measuring site.

Also some instrumental failure occured and the instrument had to be carried twice to the supplier for a long time for the reparation needed. Since the end of May 2002 the instrument is equipped with a completely new optical filter (monochomator). Since this change no major problems were encountered.

3.1.2.6 Installation of instruments and data communication

The installation of the instruments and computer needed the following general requirements:

- thermal isolation and air conditioning (about 20°C in winter, 25 °C in summer),
- remote control of the station,
- suited installation of machines and computer (independent fuse, distribution of the power needed over several phases, uninterruptible power supply UPS to protect computer and sensitive instruments from corruption or loss of data due to power line disturbance and short lasting power failures),
- short residence time in sampling tube (<10 s),
- lightning protection for cable and sampling tube entering the station.

The remote control of the instruments was realized through the installation of an ISDN connection and the standard software PC Anywhere. The performance of all of the instruments could be checked every day from the office. An extensive Labview program controlled the measurement and the calibration procedures of the N – compounds measurements instruments. On the same computer CO measurements were directly viewed. The ozone analyzer was connected to a modem managed by Meteo Swiss. Data were first collected at Meteo Swiss in Payerne and subsequently delivered to us with other local meteorological measurements.

The choice of the material used for the sampling line was very important due to the low concentrations that were present in Arosa. With exception of the NO_y - measurement the sampling air for all the instruments was provided by a single ventilator which produced a flow > 100 l/ min in a tube treated with a special aluminum coating (length 1.5 m, diameter 4 cm, equipped with a mechanical filter, material provided the company Digitel in Hegnau, Zurich). This material is supposed to be almost completely inert for all the compounds detected. This tube was followed by a glass sampling tube (diameter 4.6 cm). The air was sampled at about 4 m above the ground over the roof of the

measurement station. The sampling tubes (1/4', PFA - Teflon or steal) of the several instruments were connected to the glass tube. The amount of air going through the different instruments represented about 1/10 of the volume of sampled air. In order to avoid contaminations the instruments air exhausts were filtered with charcoal and carried outside of the measurement station at the opposite side from the sampling line. For the NO_y measurement the molybdenum (Mo) - converter was installed at a mast about 4 m above the ground over the roof of the station. With the instant conversion to NO at entrance of the sampling line the loss of NO_y – compounds in the sampling tube was avoided or strongly diminished; a 1/4' PFA - Teflon tube connected directly the converter with the NO – analyser.

3.1.3 Data availability

The measurements discussed here were performed during 24 months from September 2000 to August 2002. At first the ozone measurement was started on September 2000. From Feb 2001 also NO_x and NO_y instruments were set up. At the end of March 2001 CO measurement was started. Several interruptions occurred during the campaign. These interruptions were mainly due to instrumental problems and to a less extent to power failures during strong thunderstorms. Most affected were the NO_2 and the CO measurement (Table 3).

[%]	NO_y	NO	NO_2	O_3	CO
Sep 2000	-	-	-	100.0	-
Oct 2000	-	-	-	99.0	-
Nov 2000	-	-	-	95.0	-
Dec 2000	-	-	-	85.3	-
Jan 2001	-	-	-	97.4	-
Feb 2001	82.7	82.8	81.8	98.7	-
Mar 2001	98.8	98.9	64.1	98.4	27.0
Apr 2001	95.9	95.4	40.7	99.8	1.3
May 2001	92.3	91.9	24.2	97.4	0.7
Jun 2001	80.8	71.2	-	99.7	72.1
Jul 2001	78.8	78.8	-	98.5	45.7
Aug 2001	78.2	-	-	98.7	33.8
Sep 2001	38.9	38.5	-	98.7	29.1
Oct 2001	97.8	97.6	-	99.2	50.8
Nov 2001	82.6	82.2	63.7	91.4	81.4
Dec 2001	94.4	93.6	93.9	100.0	99.9
Jan 2002	73.1	57.1	56.5	98.9	-
Feb 2002	96.8	96.8	83.7	97.1	-
Mar 2002	99.8	99.6	-	90.7	-
Apr 2002	96.3	96.1	-	100.0	-
May 2002	99.9	99.9	-	97.1	8.53
Jun 2002	99.7	99.5	56.4	92.5	99.7
Jul 2002	95.0	92.0	64.0	97.0	81.0
Aug 2002	98.0	98.0	97.0	95.0	57.0

Table 3: Data availability for the entire measurement campaign in Arosa in %.

Table 3 shows that the data set includes 2 years of ozone measurements and approximately 1.5 years of NO and NO_y. Simultaneous measurements of all instruments are available for a periods in spring 2001, in late fall 2001 and early winter 2002 and summer 2002. If it is not specified results are presented in continental (winter) time (CET).

3.2 Chemical measurements from other sites

For the evaluation of the measurements performed in Arosa chemical data from other sites were used. Table 4 shows the location and gives basic information on their main characteristics.

Station	Parameter	Altitude m	Coordinates	Characteristics	Source
Arosa, LKO	O_3	1850	46°46' – 09°40'	Alpine, village	MeteoSwiss
Davos	O_3	1637	46°49' – 06°51'	Alpine, forest	NABEL
Chur	O_3	665	46°51' – 09°32'	Agglomeration	AfU Graubünden
Grabs	O_3, NO_2	475	47°11' – 09°26'	Rural, Rhine valley	Ostluft
Vaduz	O_3, PM10, NO_2	450	47°08' – 09°32'	Rural, Rhine valley	Ostluft
Chaumont	O_3, NO_x	1136	46°57' – 06°58'	Rural, Jura	NABEL
Jungfraujoch	O_3, CO, NO_y, NO_x	3578	46°32' – 07°59'	High Alpine	NABEL
Taenikon	O_3, NO_x	538	47°28' – 08°54'	Rural, Swiss Plateau	NABEL
Payerne	O_3, CO	490	46°48' – 06°56'	Rural, Swiss Plateau	NABEL
Payerne	O_3 profile	-	-	Lower Troposphere	Meteo Suisse
Rigi	O_3, NO_x	1030	47°04' – 08°27'	Rural, Pre Alps	NABEL
Dübendorf	O_3, NO_x	430	47°24' – 08°36'	Agglomeration	NABEL
Magadino	O_3	203	46°09' – 08°56'	Rural-agglomeration	NABEL
Monte Cimone	O_3	2165	44°12' – 10°42'	Alpine	CNR Mt. Cimone

Table 4: Chemical measurements of other stations were used in this work.

3.3 Synoptic weather classification over Switzerland

3.3.1 Introduction

The synoptic weather influences ambient air concentrations of primary and secondary pollutants. The dataset in Arosa was evaluated by applying the weather classification purposed by Schüepp. This information is contained in the Alpine Weather Statistics (SMA, 1985; Wanner *et al.* 1998). This classification is based on the daily analysis of the following 4 meteorological parameters: 1. *surface pressure gradient*, 2. *wind direction and speed at 500 hPa,* 3. *height of the 500 hPa surface over Switzerland* and 4. *baroclinicity.* Knowing these values it is possible to classify the synoptic weather type over the region of the central Swiss Alps and the Swiss Plateau in 40 different types. This region is defined as a circular area with a radius of 222 km whose centre is located at 46 ½° N and 9 °E. This large number of weather type can be reduced to 3 basic weather types and 8 extended weather types (Table 5).

The advective weather type describes weather conditions with predominantly horizontal air masses motion. The classification of this weather type is mainly based on the wind direction at the 500hPa level.

The convective weather type covers a situation in which the atmospheric motions are predominantly vertical, especially at 500 hPa. On days with cyclonic conditions (C) frictional convergence at surface results in ascent air motion: this air motion implies in the considered region adiabatic cooling, cloud formation with possible precipitation and low radiation intensity at the surface.

On days with anticyclonic conditions (H) frictional divergence at surface results in subsidence: this motion is associated with adiabatic air warming, cloud dissipation and high radiation intensity at the surface and causes high stability in the

troposphere. The class indifferent (I) includes convective days without any clear pressure level tendency. The pressure gradient between west and centre of Europe is weak (flat pressure distribution). Characteristic for this weather type is the alternation of small scale up- and down motion of air masses, cumulus clouds can be formed and very local precipitation can occur (thunderstorm).

Basic types	Extended types	Synoptic motion
I Advective	1. east (E)	NE – SE at 500 hPa
	2. south (S)	S – SW at 500 hPa
	3. west (W)	W at 500 hPa
	4. north (N)	NW – N at 500 hPa
II Convective	5. cyclonic (C)	Lifting
	6. indifferent (I)	Small – scale circulations
	7. anticyclonic (H)	Subsidence
III Mixed or vortex	8. mixed (M)	Active cyclonic or jet flow

Table 5: Weather type classification purposed by Schüepp (SMA, 1985).

Days that can not be classified into the categories advective and convective are put in a third class: this weather type mixed or vortex (M) contains days in which both vertical and horizontal motion are not negligible. Typically these days occur when an active cyclone or a front is passing through the considered area. Jet flow situations are also accounted in this type.

3.3.2 Frequency of weather types in 2000 - 2002

Table 6 and Figure 8 summarise the synoptic weather type between fall 2000 and summer 2002 in which the field measurements in Arosa were performed. The convective weather type is predominant throughout the year and exhibits a pronounced maximum in summer. Advection processes become more frequent at winter time.

% *(# days)*	Fall 2000	Winter 2001	Spring 2001	Summer 2001	Fall 2001	Winter 2002	Spring 2002	Summer 2002
East	1.1 *(1)*	4.4 *(4)*	1.1 *(1)*	0 *(0)*	1.1 *(1)*	4.4 *(4)*	3.3 *(3)*	0 *(0)*
South	17.6 *(16)*	24.5 *(22)*	6.5 *(6)*	3.3 *(4)*	8.8 *(8)*	7.8 *(7)*	8.7 *(8)*	4.3 *(4)*
West	3.3 *(3)*	12.2 *(11)*	13 *(12)*	4.3 *(4)*	6.6 *(6)*	18.9 *(17)*	4.3 *(4)*	5.4 *(5)*
North	9.8 *(9)*	13.3 *(12)*	19.6 *(18)*	14.1 *(13)*	14.3 *(13)*	16.7 *(15)*	13.0 *(12)*	8.7 *(8)*
Cyclonic	14.3 *(13)*	5.6 *(5)*	5.4 *(5)*	2.2 *(2)*	4.4 *(4)*	2.2 *(2)*	10.5 *(10)*	10.9 *(10)*
Indifferent	29.7 *(27)*	23.3 *(21)*	29.4 *(27)*	41.3 *(37)*	36.3 *(33)*	16.7 *(15)*	40.2 *(37)*	45.7 *(42)*
Anticyclonic	13.2 *(12)*	12.2 *(11)*	14.1 *(13)*	27.2 *(25)*	18.7 *(17)*	25.5 *(23)*	17.4 *(16)*	20.7 *(19)*
Mixed	11 *(10)*	4.4 *(4)*	10.9 *(10)*	7.6 *(7)*	9.8 *(9)*	7.8 *(7)*	2.2 *(2)*	4.3 *(4)*

Table 6: Extended weather types and season variability between fall 2000 and summer 2002.

The influences of synoptic weather types on the local meteorological variables are illustrated in Table 7. Temperature in Arosa is clearly higher during anticyclonic weather conditions, especially in winter temperature stay over zero degree during these weather conditions. Relative humidity also follows the same behaviour. The mean temperature value for rather seldom East advection (Figure 8) indicates that these conditions are quite extreme: so during winter this transport pattern is associated with cold and dry continental air, whereas in the other seasons temperature can increase sometimes at even higher level than during anticyclonic weather conditions.

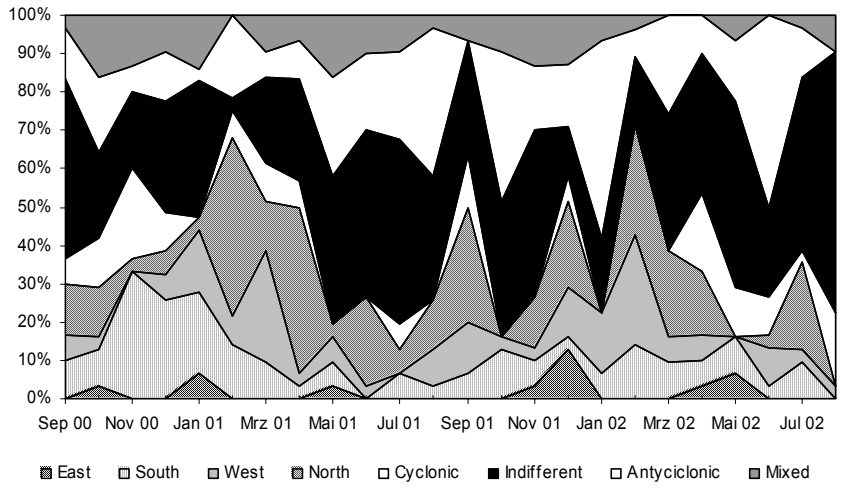


Figure 8: Extended weather type and monthly variability during the campaign from September 2000 to August 2002.

South and North advection are not always strongly influenced by the orography (this classification is mainly based on the meteorological situation at 500 hPa), however the differences between these two categories are quite pronounced (temperature and RH). During advective weather types the wind speed is usually higher. The high solar radiation can lead to a fully developped valley wind circulation during the warm season. This explains the high values of wind speed observed during convective conditions.

	Fall						*Winter*					
	P	T	RH	G*	s	f	P	T	RH	G*	s	f
	mbar	°	%	W/m^2	m/s	m/s	Mbar	°	%	W/m^2	m/s	m/s
E	810	11.8	53	384	5.2	10.7	817	- 3.5	65	382	1.7	2.3
S	807	3.9	63	277	5.5	10.9	807	- 0.1	64	218	5.3	9.8
W	814	7.1	77	269	2.9	4.3	807	- 1.95	74	264	4.0	6.9
N	814	1.2	87	296	2.4	3.6	812	- 7.0	79	289	2.4	3.4
C	805	0.6	80	264	2.8	4.5	796	- 8.4	80	392	2.3	3.2
I	816	5.9	71	397	2.2	3.4	810	- 3.6	59	260	1.8	2.5
A	821	8.5	54	505	2.0	3.0	821	2.0	52	355	2.1	3.1
M	809	3.3	76	197	3.8	7.0	810	- 3.9	78	229	1.9	2.6
	Spring						*Summer*					
	p	T	RH	G*	s	f	P	T	RH	G*	S	f
	mbar	°	%	W/m^2	m/s	m/s	Mbar	°	%	W/m^2	m/s	m/s
E	816	8.2	65	412	2.1	3.1	-	-	-	-	-	
S	810	5.2	61	601	4.5	8.2	813	8.3	81	358	3.7	6.5
W	805	-0.1	73	475	3.6	5.8	818	8.5	75	504	2.5	3.7
N	808	-3.4	85	542	3.0	4.4	817	4.9	79	470	3.1	4.8
C	803	-1.9	76	562	3.2	5.0	809	5.9	91	449	2.0	2.9
I	810	3.7	71	566	2.9	4.8	816	10.2	70	579	3.0	4.7
A	819	7.8	58	711	2.3	3.5	821	14.7	61	760	2.9	4.4
M	810	3.8	76	593	3.6	6.0	813	7.9	86	396	2.6	4.3

Table 7: Seasonal mean values for each extended weather type (meteorological measurements in Arosa in 2001).

3.4 Backward trajectories

3.4.1 Wind fields

Three dimensional (3-D) backward trajectories ending in Arosa were calculated in order to investigate the ozone concentration measured in Arosa in respect to origin of air mass. Meteorological wind fields from the European Center for Medium range Weather Forecast (ECMWF) were applied. Fields were available on a horizontal resolution of 1°x1° geographical grid covering the whole northern hemisphere. The data used have a vertical resolution of 60 layers whereby about 13 layers are situated in the lowest "boundary layer" (p > 800 hPa) and totally 30 layers describe the troposphere (p > 200 hPa). The temporal resolution of available wind fields amounts to 6 hours. Compared with the outputs of free running meteorological models, ECMWF analyses are believed to be preferable, because they remain consistent with observed meteorology. In addition ECMWF wind fields allow calculating 10 days backward trajectories.

3.4.2 Trajectory calculation

Three dimensional 10 days backward trajectories used in this work were calculated by applying the model LAGRANTO (LAGrangian Analysis Tool) (Wernli & Davies, 1997). Everyday at 06 UTC a bundle of backward trajectories was started at 800 hPa. Beside the trajectory starting at the grid point of the measurement site four additional trajectories were calculated. They were displaced by ±0.5° of latitude and longitude from the monitoring site. The calculation and interpolation provide information about trajectories position (longitude, latitude, pressure) with a time step of 2 hours.

A backward trajectory starting time of 06 UTC was chosen. During daytime the local influence due to polluted air masses is largest when strong up slope can occur (section 2.3.3). To avoid / reduce these possible influences trajectories were chosen to arrive at night - early morning when down slope flow predominates at mountain sites. Real topography and model topography (understood as altitude) in Arosa does not differ considerable. The 800 hPa chosen for the starting point of the backward trajectories corresponds to a height above sea level that is only slightly higher than the real altitude of the station and or the height of the model topography. The Arosa basin surrounded by the high mountain peaks (section 3.1.1) is instead not reproduced by the simplified Alps topography included in the model. The flow pattern in the proximity of the Alps is therefore only a simplified description of the reality. Although analysed wind fields were used differences between simulation and real air flow might exist. Generally these errors are becoming larger by increasing duration of the backward trajectories. It is generally accepted that for simulation longer than 10 days the accuracy of the trajectories rapidly decreases (Wernli, IACETH, personal communication). Detailed and comprehensive information about computation, accuracy and application of trajectories can be found elsewhere (Stohl, 1998). Most studies agree that three dimensional trajectories are the most accurate trajectory type. Errors of 20% of the distance travelled seem to be typical for trajectories computed from analyzed wind fields (Stohl, 1998). The coarse spatial resolution of the wind fields can not describe small scale processes (e.g. upslope wind and local convection) which lead to errors in the modelled air parcels flow.

3.4.3 Residence time

To calculate the residence time of air parcels over the polluted European continent it was necessary to define a clear area. As European “polluted” continent was defined a region including England, central Europe, southern Europe, part of eastern Europe and the southern part of Scandinavia which covers the latitude region from 35°N to 60°N and the longitude region from 10°W to 30°E. Maps of ozone precursor emissions (Figure 10) clearly show that this region includes the strongest emissions sources located on the European continent. In addition to this space window a land – sea mask was considered as a criteria for the computation of the residence time. Residence time was thus only taken into account if trajectories were located on the European mainland. The daily residence time was calculated by averaging the residence times of the 5 trajectories started n the bundle. In summer air masses stayed on average over Europe for a longer period than in winter time. For example residence class 0-1 day in summer only contains 2 events whereas 24 were found in winter (Figure 9).

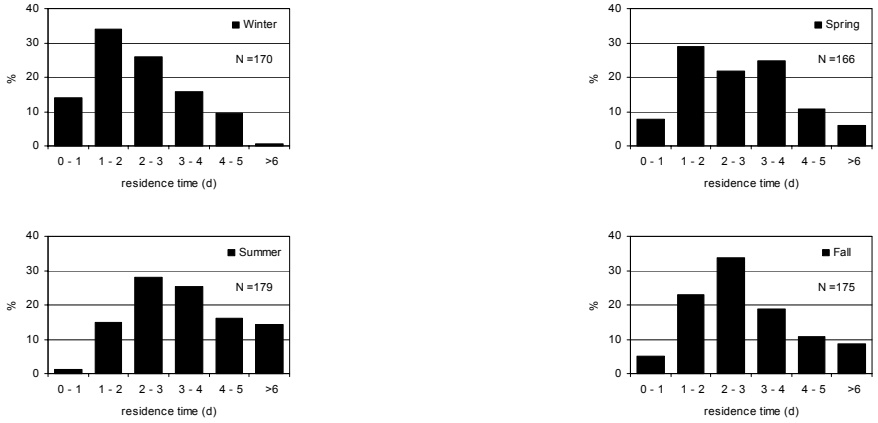


Figure 9: Frequency of air parcel residence time calculated from trajectories between September 2000 and August 2002, months are grouped into climatological season.

3.4.4 Surface solar radiation fields from ECMWF

In order to quantify the weather condition along the trajectories, 2-dimensional surface solar radiation (SSR) fields from ECMFW were used. Available were fields for June and July 2001 and 2002. The spatial resolution of the model data was 1°x1°. These fields are forecasted and available every 12 hours (at 00 UTC and 12 UTC) and contain information about the total amount of surface solar radiation during the last 12 hours at a specific grid point. In Figure 10 one can recognize structures giving valuable information like north to south solar radiation gradient and cloud coverage e.g. as consequence of a frontal system. The information about solar radiation is potentially important in respect to photochemical history of an air parcel. Solar radiation data were allocated along the trajectory as follow: the field available at 12 UTC was attributed to the time period 02-12 UTC whereas the field available at 00 UTC was attributed to the time period 14-00 UTC. In other words for a backward trajectory ending at 06 UTC on the 1st of June the SSR values at -2 hours (4 UTC) and -4 hours (2 UTC) originate from the field of the 1st June 12 UTC; SSR values at - 6 hours (00 UTC), - 8 hours (22 UTC) to -16 hours (14 UTC) originate from the field of 30 May at 00 UTC and so on for the following days.

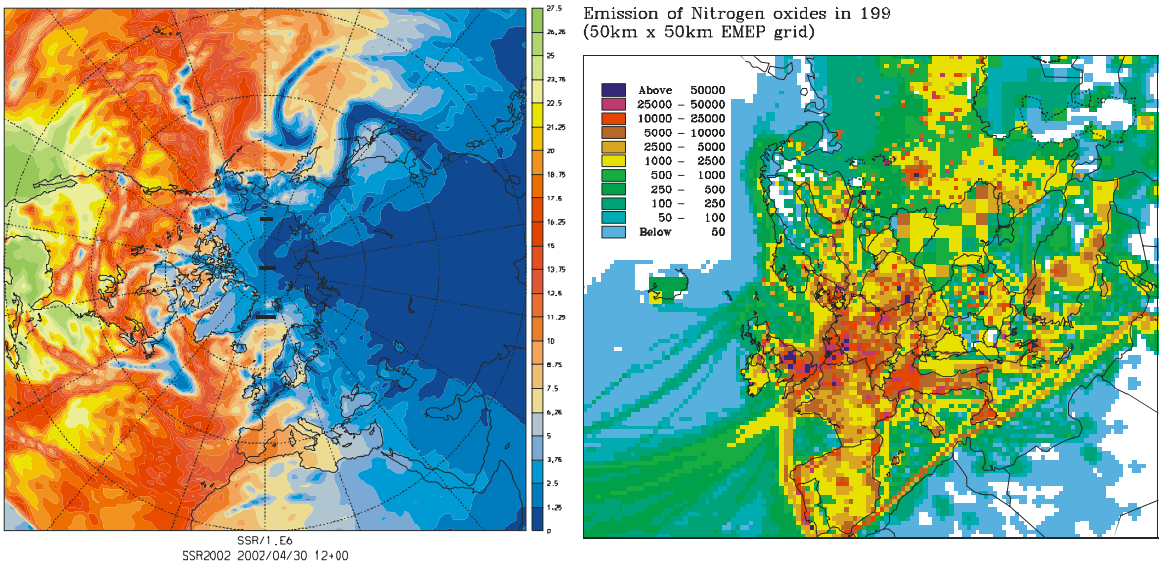


Figure 10: left: surface solar radiation fields from ECMWF, northern hemisphere field of the 30th of April 2002 at 00 UTC, 10^6 joule/m2, and right: EMEP emissions data base for NO_2 in tones per year (1998).

4 Overview of the measurements in Arosa

4.1 Introduction

This chapter is devoted to condensed summary of the measurements performed in Arosa. Table 9 summarises all the measurements performed and gives the main statistical parameter in a monthly basis. Statistical values are given only if the data availability within a month was reasonably high. The data shown here are processed from hourly averaged data. The monthly mean data are summarised in Table 9. The chapter starts with a description of the local wind system and its relation to the synoptic weather classes, followed by a documentation of the very local influences. In 4.4 we discuss the seasonal variation of ozone, NO_y and CO.

If it is not specified results are presented in local winter time (CET).

4.2 Description of the local wind system

Attention is given to the circulation that occurs in the basin at the end of the valley, where the investigation site is located. In a previous work carried out in the Arosa basin the wind system was investigated in detail (Graber, 1985). The measurement station in Arosa being located in a basin is not directly influenced by the geostrophic wind since mountain peaks protect the basin. Table 8 shows for the three mountain stations Arosa, Weissfluhjoch (2690 m) and Jungfraujoch (3580 m) the average monthly wind speed. Arosa is clearly characterised by lower mean speed value compared to the 2 other stations. The difference is less pronounced in summer. In this season convective weather type is more frequent and thermally driven valley and up - slope winds can fully develop in the Plessur valley. Table 8 also indicates that during extreme conditions Arosa can be affected by wind as strong as on the Weissfluhjoch, however never values as high as on the Jungfraujoch are reached.

	Mean Arosa [m/s]	Mean WFJ [m/s]	Mean JFJ [m/s]	Max Arosa [m/s]	Max WFJ [m/s]	Max JFJ [m/s]
Jan	2.4	5.5	8.0	19.6	15.7	32.4
Feb	2.9	5.6	10.6	20.4	19.5	33.5
Mar	3.2	5.7	9.3	17.4	21.3	36.7
Apr	2.9	5.5	8.7	11.2	20.9	29.3
May	2.9	4.5	9.5	14.8	18.8	31.3
Jun	2.9	4.3	8.0	12.1	17.4	37.8
Jul	3.0	3.9	7.3	13.7	15.3	26.7
Aug	2.8	2.6	7.0	11.0	11.5	19.6
Sep	2.6	4.7	7.5	13.8	17.3	26.2
Oct	2.9	4.3	8.5	14.4	16.6	31.6
Nov	2.8	5.3	8.4	17.3	20.8	31.6
Dec	2.5	6.0	9.0	17.3	18.6	31.3

Table 8: Monthly mean and monthly maximum of wind speed registered in Arosa (2030 m), on the Weissfluhjoch (WFJ: 2690 m) and on the Jungfraujoch (JFJ: 3580 m) (calculated from hourly average data from September 2000 to August 2002).

The valley floor below Arosa is influenced by mountain and valley winds that develop in the Plessur valley. Graber (1985) observed at the valley floor of the Arosa basin

the development of a morning NE valley wind during summer. This wind lasted normally until late afternoon and was then regularly replaced by a SW mountain wind after sunset. The mountain wind instead dominated during winter time the valley floor below Arosa through all the day. The measurement station in Arosa is located 200 – 300 m above the valley floor and is exposed to up and down slope wind. These might occur through the entire year (Graber, 1985). These are however most pronounced in case of fair weather in summer. In Arosa shortly after sunrise a gently up slope wind usually from SE was observed which turned to a stronger valley wind from E – NE (Figure 11).

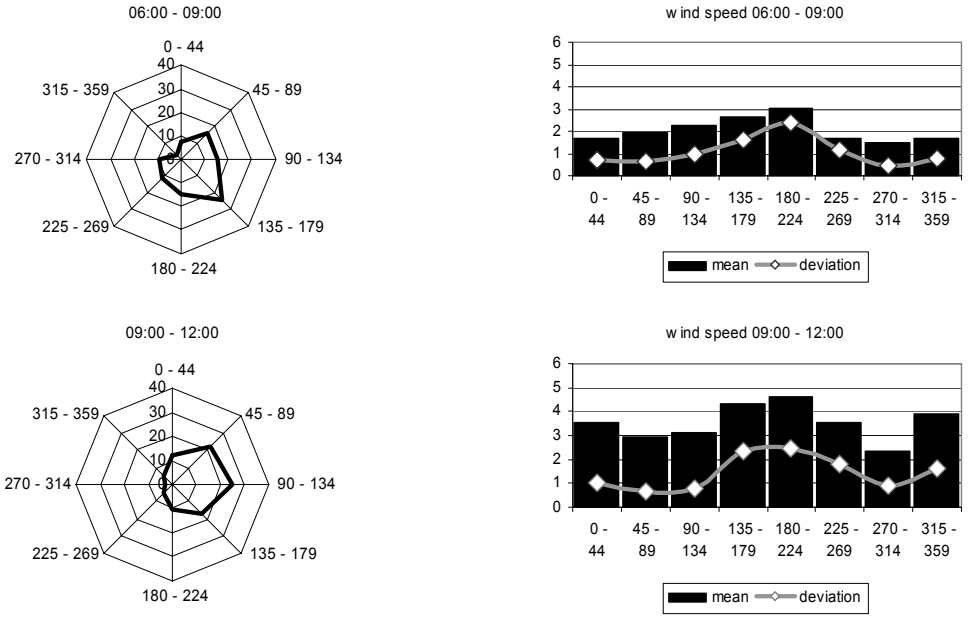


Figure 11: Morning upslope wind and valley wind in Arosa-Tschuggen in case of good weather conditions (daily average of relative humidity <80%, summer 2001). Wind direction (left) and wind speed and its standard deviation (m/s, right).

When solar radiation is not equally distributed to the valley slopes cross valley winds can develop in addition to the valley – and slope winds (Barry 1981). This is the case for the station in Arosa. Graber (1985) showed the occurrence of strong NW cross valley wind in the afternoon in Arosa due to the enhanced sun exposition of the slopes on the East part of the Arosa basin. These cross valley winds usually occurred in summer and late spring (Figure 12).

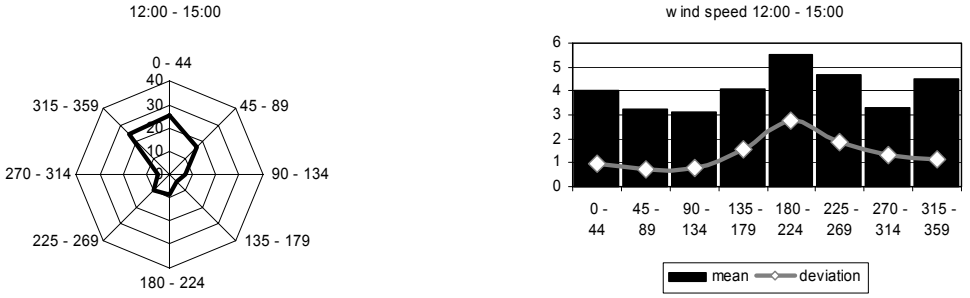


Figure 12: Afternoon cross valley wind in Arosa-Tschuggen in case of good weather conditions (daily average of relative humidity <80%, summer 2001). Wind direction (left) and wind speed and its standard deviation (m/s, right).

Although these wind directions were often not parallel to the valley axis, they could be considered representative for the general upslope system in the Plessur valley (Stahelin *et al.*, 1994).At the investigation site during night a weak wind (< 2 m/s) normally dominates. The station in Arosa, located 200 – 300 m above the valley floor, was not directly influenced by the mountain wind. Wind directions from the W to NE section prevail at the station. Graber (1985) performed wind profile sounding and concluded that the Tschuggen can be influenced by an anti mountain wind which compensate the main valley outflow.

Measurements in Arosa also showed that the influence of the synoptic weather can occasionally be so strong that the valley circulation did not develop (Figure 13). During strong advective weather (except West) the influence was rather pronounced. By convective weather type wind directions, which were connected with the valley wind system seemed to prevail (especially by indifferent and anticyclonic conditions).

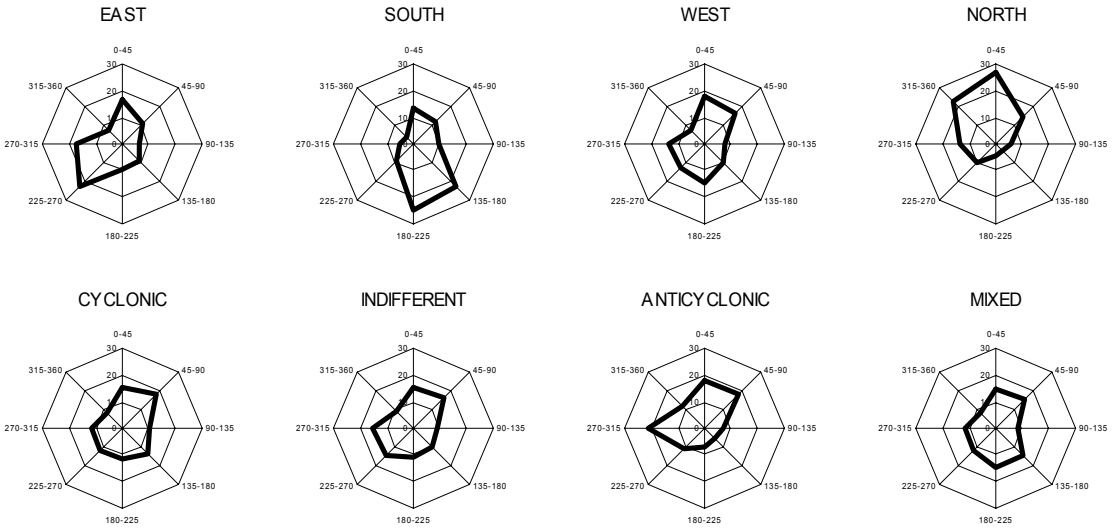


Figure 13: wind direction frequency for each extended weather type (September 2000 to August 2001).

4.3 Dominant influence of local emission during winter

The seasonal variation in NO reflects the influence of anthropogenic activity in Arosa on the measurement station. As nitrogen oxides are released into the troposphere mainly in form of NO. The highest values in NO concentrations were generally found during winter (from December to March) and were related to local emissions during the ski season (Table 9). The influence of local emissions was usually restricted to the day time. Figure 14 shows however the strong impact of the passage of a machine, preparing the ski slope during night time, on the concentrations of nitrogen compounds (slope 20-30 m away from the station).

Such events clearly characterised all the period of ski season, especially in the late afternoon and at night. These very short events were clearly recognisable. These values were removed from the data set.

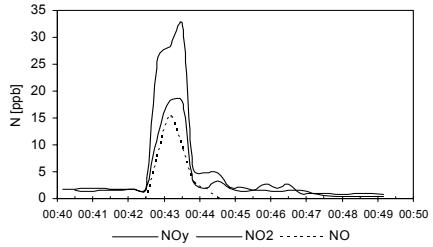


Figure 14: Emissions caused by machines preparing ski slopes recognizable in a strong increase in NO concentration (14th of January 2002 short after midnight). Such disturbances lasted only few minutes.

4.4 Seasonal variation of measured compounds

4.4.1 Ozone

The mean seasonal cycle shows a spring ozone maximum accompanied by extended high values during summer months (Figure 15 and Table 9). A spring maximum was coincident with May 2001 and with April 2002 (55.8 ppb, 57.4 ppb respectively). The mean ozone values were lowest in the cold season. These were found in October (2000) and in November (2001) (37.6 ppb, 36.3 ppb respectively). The deviation from the mean within a month was also depending on the season. During the warm season this deviation was clearly larger than in fall and winter due to contribution of photochemical ozone production. The annual variation of ozone in Arosa was in agreement with other results collected at rural stations in central Europe (Scheel *et al.*, 1997). In the western edges of Europe and at high latitude (e.g. rural site in Scandinavia) there are sites showing a summer minimum after a spring maximum. This can be explained by the dominance of ozone photolysis in low NO_x conditions (Solberg *et al.*, 1997). Moving towards central Europe (which includes Arosa) the spring maximum is instead followed high concentrations in summer and by a broad decrease in ozone towards the autumn (Scheel *et al.*, 1997).

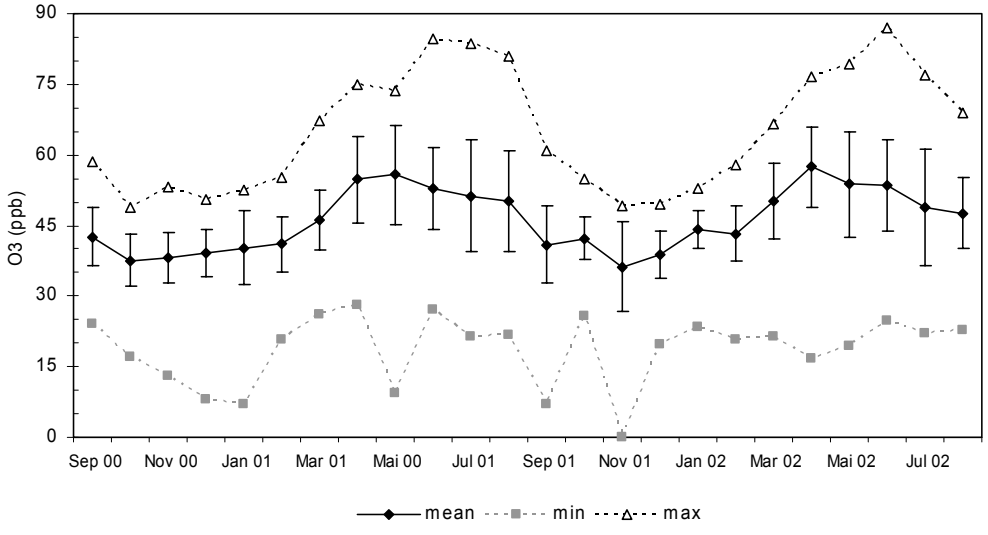


Figure 15: Ozone concentration measured in Arosa from September 2000 to August 2002. Bars denote standard deviation.

Table 9: Summary of O_3, NO_y, NO_2, NO and CO measurement in Arosa.

[ppb]	Sep 2000	Oct 2000	Nov 2000	Dec 2000	Jan 2001	Feb 2001	Mar 2001	Apr 2001	May 2001	Jun 2001	Jul 2001	Aug 2001	Sep 2001	Oct 2001	Nov 2001*	Dec 2001	Jan 2002	Feb 2002	Mar 2002	Apr 2002	May 2002	Jun 2002	Jul 2002	Aug 2002
	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3	O3
mean	42.6	38.3	39.2	39.5	40.3	40.9	46.2	54.7	55.8	52.9	51.4	50.1	40.8	42.3	36.3	38.7	44.1	43.3	50.2	57.4	53.7	53.5	50.1	47.6
st.dev	6.1	5.4	5.3	5.0	7.9	5.8	6.4	9.1	10.5	8.6	12.0	10.8	8.1	4.6	9.7	5.1	3.9	5.8	7.9	8.5	11.3	9.6	9.8	7.5
median	42.9	38.2	39.2	39.6	42.5	41.6	46.2	53.9	57.7	54.0	51.9	49.6	40.1	42.8	37.7	39.5	44.7	43.8	51.8	57.4	54.2	54.3	50.0	47.6
max	58.6	48.9	53.3	50.5	52.6	55.0	67.1	75.1	73.6	84.5	83.7	80.9	60.8	55.0	49.2	48.4	52.9	57.8	66.6	76.5	79.3	86.9	76.8	68.8
min	24.0	17.2	13.0	8.1	7.1	20.7	26.0	28.1	9.4	27.0	21.3	21.9	7.14	25.6	0	19.6	23.4	20.7	21.5	16.6	19.3	24.8	22.1	22.5
Q25	38.4	34.6	36.1	37.0	37.5	37.4	42.6	48.3	51.6	47.4	42.7	43.6	36.3	39.7	32.8	34.9	41.8	39.2	43.1	52.1	46.3	48.3	43.1	43.2
Q75	47.0	41.4	41.7	42.2	45.0	45.3	49.6	62.8	63.3	58.2	59.4	57.6	47.0	45.5	43.8	42.6	47.1	47.2	55.5	63.1	62.3	59.3	56.1	52.8
[ppb]	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy	NOy
mean	-	-	-	-	-	3.43	2.40	2.66	2.44	2.12	2.69	2.19	1.91	1.50	2.00	2.66	2.13	3.11	2.36	2.78	2.38	3.04	1.98	1.96
st.dev	-	-	-	-	-	2.35	1.33	1.52	1.19	1.45	1.46	1.32	1.23	0.91	2.14	1.74	1.81	2.67	1.02	1.09	1.34	1.87	0.85	0.87
median	-	-	-	-	-	2.73	2.07	2.38	2.17	1.78	2.59	1.85	1.59	1.32	1.27	2.37	1.51	2.42	2.34	2.63	2.03	2.65	1.87	1.77
max	-	-	-	-	-	14.8	7.30	9.05	7.24	9.61	7.13	7.19	7.42	5.54	17.11	10.74	11.39	18.93	9.58	9.04	8.26	9.47	5.75	8.61
min	-	-	-	-	-	0.54	0.48	0.49	0.87	0.33	0.39	0.39	0.37	0.27	0.22	0.21	0.25	0.19	0.45	0.89	0.46	0.37	0.16	0.41
Q25	-	-	-	-	-	1.80	1.41	1.48	1.59	1.08	1.34	1.18	1.17	0.81	0.71	1.36	0.90	1.38	1.62	2.05	1.37	1.70	1.39	1.32
Q75	-	-	-	-	-	4.31	3.20	3.62	2.94	2.84	3.64	2.98	2.47	1.88	2.29	3.35	2.78	3.85	2.87	3.23	3.08	3.63	2.41	2.47
[ppb]	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO
mean	-	-	-	-	-	0.40	0.33	0.29	0.17	0.11	0.13	-	0.15	0.11	0.23	0.49	0.43	0.72	0.41	0.23	0.15	0.09	0.07	0.08
st.dev	-	-	-	-	-	0.55	0.45	0.47	0.12	0.18	0.20	-	0.24	0.17	0.52	0.93	0.79	1.21	0.80	0.41	0.38	0.10	0.11	0.12
median	-	-	-	-	-	0.17	0.13	0.10	0.04	0.06	0.07	-	0.04	0.02	0.02	0.04	0.09	0.24	0.13	0.08	0.06	0.06	0.04	0.03
max	-	-	-	-	-	4.39	2.77	3.68	1.12	3.22	2.16	-	1.43	1.11	6.00	5.99	3.79	10.2	7.76	4.15	4.45	1.18	1.05	1.25
min	-	-	-	-	-	0.03	< 0.01	< 0.01	< 0.01	0.01	0.02	-	0.01	<0.01	< 0.01	<0.01	<0.01	0.03	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Q25	-	-	-	-	-	0.08	0.05	0.01	0.01	0.04	0.05	-	0.02	0.01	0.01	0.02	0.02	0.10	0.04	0.03	0.02	0.04	0.02	0.02
Q75	-	-	-	-	-	0.52	0.41	0.38	0.10	0.12	0.13	-	0.18	0.13	0.20	0.51	0.37	0.86	0.46	0.24	0.11	0.10	0.09	0.1
[ppb]	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2	NO2
mean	-	-	-	-	-	1.98	1.44	0.81	0.54	-	-	-	-	-	1.14	1.63	1.39	2.43	-	-	-	1.12	0.75	0.67
st.dev	-	-	-	-	-	1.83	1.19	0.86	0.71	-	-	-	-	-	1.28	1.56	1.30	2.30	-	-	-	0.54	0.46	0.53
median	-	-	-	-	-	1.35	1.07	0.39	0.26	-	-	-	-	-	0.67	1.15	0.90	1.79	-	-	-	0.94	0.62	0.49
max	-	-	-	-	-	11.55	6.39	4.46	4.48	-	-	-	-	-	6.88	9.68	5.94	15.0	-	-	-	3.08	6.22	6.20
min	-	-	-	-	-	0.16	0.13	0.10	0.05	-	-	-	-	-	0.04	0.04	0.07	0.10	-	-	-	0.39	0.18	0.16
Q25	-	-	-	-	-	0.77	0.62	0.24	0.16	-	-	-	-	-	0.25	0.55	0.40	0.85	-	-	-	0.72	0.45	0.36
Q75	-	-	-	-	-	2.55	1.90	1.03	0.59	-	-	-	-	-	1.52	2.18	2.03	3.17	-	-	-	1.38	0.90	0.80
[ppb]	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO
mean	-	-	-	-	-	-	202.1	-	-	138.8	151.0	150.9	-	144.2	166.0	151.9	-	-	-	-	-	135.4	134.9	117.1
st.dev	-	-	-	-	-	-	14.8	-	-	19.0	16.4	16.6	-	27.2	49.3	25.5	-	-	-	-	-	14.8	10.9	12.0
median	-	-	-	-	-	-	199.6	-	-	135.7	150.5	147.7	-	145.5	153.0	151.3	-	-	-	-	-	132.1	134.0	116.1
max	-	-	-	-	-	-	251.0	-	-	225.6	201.4	266.6	-	232.4	425.7	279.6	-	-	-	-	-	196.2	179.8	162.9
min	-	-	-	-	-	-	166.0	-	-	103.4	114.4	107.2	-	97.5	113.1	89.6	-	-	-	-	-	91.8	106.2	92.0
Q25	-	-	-	-	-	-	194.0	-	-	125.9	141.2	141.5	-	131.3	137.8	133.8	-	-	-	-	-	124.5	127.0	109.1
Q75	-	-	-	-	-	-	207.1	-	-	146.0	158.2	159.5	-	160.7	175.0	166.7	-	-	-	-	-	143.4	142.0	123.4

The spring maximum occurs in the entire northern hemisphere. One of the most important reasons for this maximum is the accumulation of precursors in the atmosphere in winter time which leads to high ozone concentrations as soon as photochemical activity is fully activated. A comprehensive description on origins of this spring maximum can be found elsewhere (Monks, 2000). Figure 16 compares the monthly averaged ozone in the period 1989-1991 (Staehelin *et al.*, 1994), and in the period 1996-1997 (Pochanart *et al.*, 2001) with measurements performed in this study. The monthly averages of ozone did not show any decrease during the total range of time (1989 – present) despite decreases in ozone precursor emissions in Switzerland and Central Europe (chapter 1). The slightly higher concentrations found in this study can be probably attributed to the different location where measurements were performed (1989-1991 and 1996-1997 measurements were performed in the nearby village). The result is not completely surprising according to results shown by a recent study in which ozone measurements at different NABEL stations between 1991 and 1999 showed a tendency of decreasing of ozone extremes (low value in urban area and high value in rural area) together with a significant increase frequency in ozone concentration in the range between 45 and 55 ppb. This change in the ozone concentrations frequency distribution finally led significant increase in background concentration of about 1 ppb/year. The authors explained part of the result by reduction in pollutant emissions (Bronnimann *et al.*, 2002).

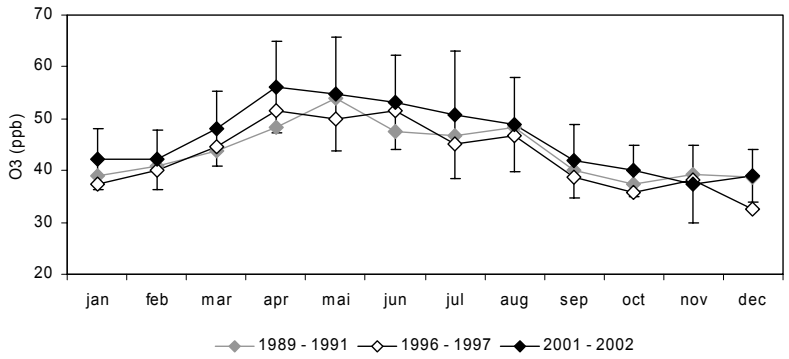


Figure 16: Comparison of monthly mean of ozone concentration in Arosa for the measurement in 1989-1991 (Staehelin, *et al.,* 1994), 1996-1997 (Pochanart *et al.* 2001) and 2000-2002 (this study).

4.4.2 Total reactive nitrogen

At a remote alpine site like Arosa NO_y concentrations were expected to be lower during winter months because of the strong temperature inversions during that time. The ratio (calculated from mean value) of about 2.6 - 3 between NO_y in Arosa and Jungfraujoch shows a strong increase during December and February, i.e. during the ski season, indicating the strong influence of local emissions. This result was further confirmed by the maximum values which were highest in the winter season (> 10 ppb, Table 9). The slightly lower values of the ratio between NO_y in Arosa and NO_y at Jungfraujoch in July and August 2002 (compared with 2001) are associated to the low NO_y concentrations measured in Arosa during that period (Table 9) and could be related with the problems encountered with the Mo converter middle of July 2002 (see 3.1.2.4) which possibly resulted in a diminished conversion in NO_y compounds.

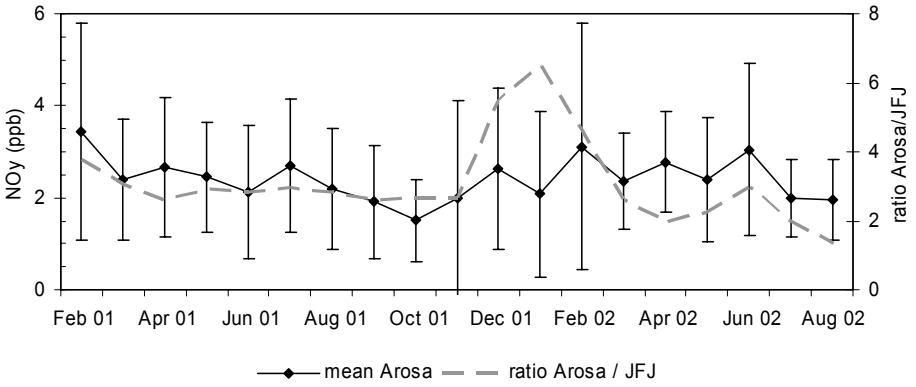


Figure 17: NO_y in Arosa (monthly mean) with standard deviation, dotted line gives ratio between NO_y in Arosa and Jungfraujoch.

4.5 Carbon monoxide

In section 3.1.2.5 we reported on problems encountered with the CO measurements which strongly affected the availability of data. Compared to measurements at Jungfraujoch, measurements in Arosa were slightly higher. This is consistent with the vertical distribution of CO in the lower troposphere showing decreasing concentrations with increasing altitude (Forrer *et al.*, 2000) (Figure 18). This tendency is however not so pronounced as for other primary pollutants or for NO_y as the considerable higher lifetime of CO in the atmosphere leads to higher background concentrations (Derwent *et al.* 1998).

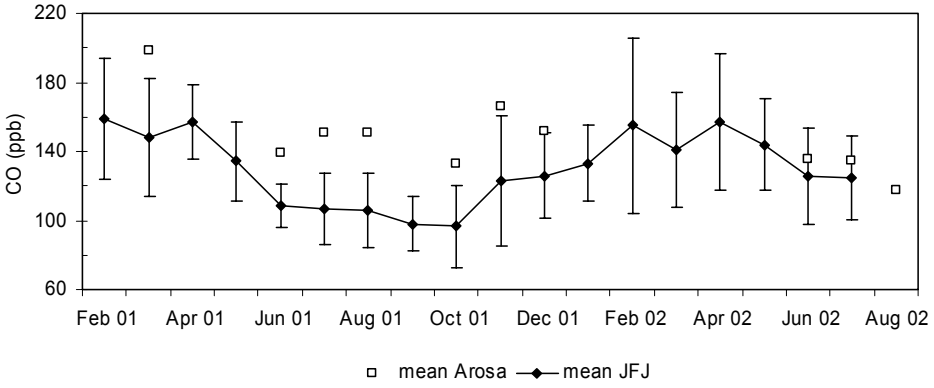


Figure 18: CO measurements in Arosa and Jungfraujoch between February 2001 and August 2002

The relatively sparse measurements in Arosa point to a small annual variation in CO concentration which is a sign of stronger boundary layer influence at this site than at Jungfraujoch. In the latter station annual CO variation better agrees with the annual variation found in typical clean air masses at Mace Head (Ireland, sea side) showing a minimum in summer (as a consequence of oxidation) and maximum in winter (Derwent *et al.*, 1994).

5 Selected case studies

Primary and secondary pollutant concentrations at an Alpine site such as Arosa are determined by emissions, dispersion and transport and photochemistry leading to the transformation of primary pollutants (section 2.1). This chapter presents the interactions between air pollutant chemistry and particular weather features, which determines the transport. The discussion of the selected case studies starts with the description of the synoptic weather conditions. The analysis also includes air pollutant measurements from other sites as well as trajectory calculation.

In section 5.1 measurements in November and December 2001, showing the strong influence of inversions and fronts, are analyzed in detail. Strong inversion layers over the polluted plain regions (e.g. the Swiss Plateau) can strongly reduce the transport of primary pollutants to high altitude (Dütsch, 1985) whereas fronts often result in an upward transport of air from the planetary boundary layer. In case of strong subsidence during an extremely strong inversion regime Arosa shows early morning similar O_3 and NO_y concentrations as the Jungfraujoch while a comparison of CO concentration in Arosa during two fronts cases with measurements performed during an airborne campaign (Huntrieser *et al.* 2002) reveals the possibly strong effect of the Alpine orography on the uplifting of boundary layer air. However high peaks of pollutants at high alpine stations are not always directly caused by frontal passages as will be discussed in a case study for 12th - 15th of November 2001. In section 5.2 the influence of the stability of the lower atmosphere in winter on ozone is generalized by the discussion of a relationship between temperature and ozone differences between Arosa and Chur. Using measurements from the NABEL network it is shown that the influence of temperature inversions and advective weather is not only restricted to low altitude stations close to emission source. This influence clearly affects on a similar way high alpine station like Arosa and Davos and is still clearly recognisable up to the Jungfraujoch.

In section 5.3 the influence of south foehn on measurements at the site Arosa and in the Rhine Valley is described in details: the foehn flow was found to transport ozone rich air to the station during the photochemically active season. Backward trajectories documented that air parcels originated over the Po basin. Thus the foehn does not only affect well exposed stations on mountain peaks (Forrer *et al.* 2000; Zellweger *et al.* 2002) or at lower altitude (Baumann *et al.* 2001; Seibert *et al.*, 2000) but can obviously descend in the Arosa basin when passing the Alps. The discussion about a comparison between ozone concentration in Arosa and Mt. Cimone (2165 m, south of the Po basin) during foehn events provide evidence for the possible processes occurring in an air parcel travelling from the Tyrrhenian Sea over the Po basin to Arosa.

Section 5.4.1 contains the discussion of a typical summer ozone episode during a high pressure situation which induced a day after day increase in ozone concentration in Arosa which is only slightly lower than at the low altitude rural station Taenikon (Swiss plateau). Low ozone concentration at the end of this event might be interpreted as undisturbed from the European emission as they were caused by large scale transport of air from high altitude and high latitude. In contrast low ozone during front events were mainly determined by ozone loss processes (section 5.4.2).

5.1 Influence of inversions and front events

5.1.1 Overview

The synoptic weather condition of this case study in November 2001 is summarized in Table 10. In the first part of the period the influence of an anticyclon located over the Alps led to strong subsidence at 500 hPa and good weather conditions in Arosa. On the 5th of November this weather condition suddenly changed due to a disturbance approaching from NW associated with a low pressure system located over Scandinavia. From the 7th advective weather situations prevailed and 3 frontal systems passed trough Switzerland causing typical bad weather in Arosa. In a second part of this period from the 16th more convective weather prevailed. This fair weather period was ended on the 23rd by the passage of a cold front associated with a strong north foehn. In the following day weather was characterised again by the passage of two other fronts.

	Weather type	Δ T $_{a-c}$	Front 00_12	Front 12_00	Altitude of fog layer at Säntis (m)	RH in Arosa (%)	T in Arosa (C°)	G in Arosa (W/m2)
03.11.2001	H	3.7			1000	48	6.5	425
04.11.2001	H	2.3			700	51	7.3	421
05.11.2001	S	-4.7	C		2100	82	0.9	256
06.11.2001	I	-9.1			2200	91	-1.2	150
07.11.2001*	M	-6.6	W		-	90	-0.1	200
08.11.2001	W	-4.8		C	-	76	1.1	304
09.11.2001*	N	-11.1			-	89	-8.9	147
10.11.2001*	I	-9.0			1800	72	-7.6	418
11.11.2001	I	-1.9			1000	61	3.0	181
12.11.2001*	M	1.4			-	84	2.6	80
13.11.2001*	N	-5.3		C	-	95	-3.6	149
14.11.2001*	S	-8.9			-	92	-7.8	163
15.11.2001	I	-1.0			1400	58	-3.0	391
16.11.2001	E	4.4			1000	19	3.4	389
17.11.2001	H	8.7			1000	23	5.0	371
18.11.2001	I	-0.4			700	39	1.0	357
19.11.2001	M	0.5			900	62	-1.8	326
20.11.2001	I	-1.2			1200	48	-1.3	364
21.11.2001	H	4.1			1400	28	1.4	362
22.11.2001	I	2.4			1000	37	-0.4	297
23.11.2001*	M	-10.6		C	-	87	-10.0	119
24.11.2001*	I	-7.8			-	84	-8.7	215
25.11.2001*	I	-2.7		W	-	94	-2.8	175
26.11.2001*	I	-3.1			-	87	-0.4	239
27.11.2001*	I	-4.2	C		-	89	-2.0	166
28.11.2001*	I	-7.2			-	90	-5.0	198

Table 10: *Days with precipitation in Arosa, weather type by Shüepp (see also Table 5), temperature difference between Arosa and Chur (hourly average between 10 and 16), front passage in Zurich between 00 and 12 CET resp. 12 and 00 CET (AWS: parameter 18 and 21, C=cold front, and W=warm front warm), upper limit of fog layer (in meter, determined at 09, according to parameter 27 AWS).

Figure 19 shows the measurements for ozone, CO, NO_y, NO and NO_2 for the selected part of November 2001 and provides a first overview how the meteorological situation described above influences air pollutant concentration at the receptor site. More variable trace gas concentration in the first part from the 5th during bad weather, a second more quiet period where ozone concentrations were significantly

higher and primary pollutant concentrations were significantly lower and a third part where pollutant concentrations clearly increased again.

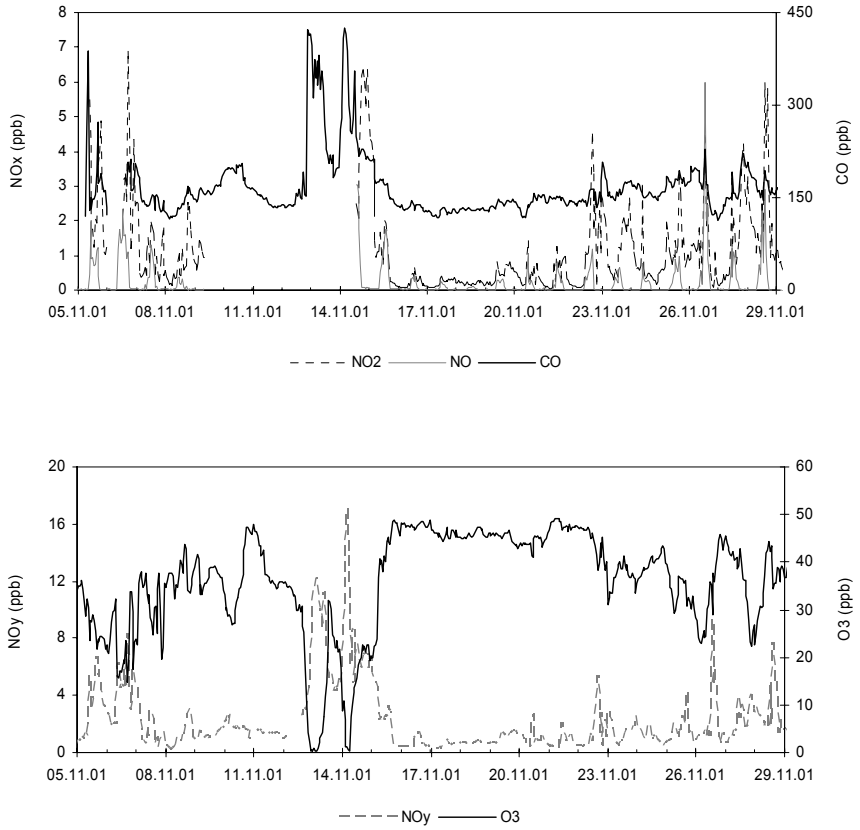


Figure 19: Time series of ozone, NO, NO_2, CO, NO_y and O_3 between the 5th and the 29th of November 2001. No NO and and NO_2 measurements between the 9th and the 14th due to failure of analyzer.

5.1.2 Influence of inversions

5.1.2.1 Event of the 5th and 6th of November 2001

Temperature differences between Arosa (2035 m) and Chur (555 m) show that there was no temperature inversion between both locations (Table 10). The mean temperature was rather high for such a bad weather situation and might be explained by the extremely good weather prevailing in Arosa until the 5th. Meteorological observation at the Säntis (2490 m) indicated that on the morning (at 09 CET) of both days the upper limit of the fog layer was 2100 - 2200 m and thus slightly higher than the altitude of Arosa (Table 10). The temperature difference between the closely located mountain peak Weissfluhjoch (2690 m) and Arosa suggests that during day time on the 5th (-2.3°C) and on the 6th (-0.9°C) a weak temperature inversion thermally decoupled the two locations. This is further supported by comparing the hours of sunshine observed at Weissfluhjoch (4.0 h on the 5th and 5.3h on the 6th) with the low values of incoming solar radiation in Arosa (Table 10). Payerne soundings from Meteo Swiss also indicate that during these 2 days a temperature inversion was localized at about 2000 m. The cold front registered in Zurich at about 12 CET of the 5th obviously did not directly reach Arosa which is confirmed by the

lack of precipitation during these 2 days. The chemical measurements in Arosa show however that ozone decreased from about 35 to less than 20 ppb in these 2 days (Figure 20). At Jungfraujoch (3580 m) no ozone decrease was detectable. The measurement site in Arosa (2035 m) was under the influence of an inversion layer localized above the measurement station. The exposure to air trapped below the inversion layer was certainly more pronounced on the 6th how it suggested by the similarity in ozone at the stations Arosa and Taenikon (Figure 20).

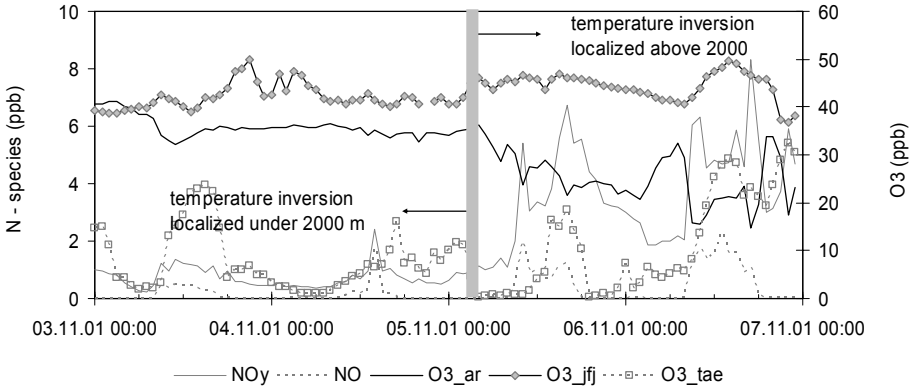


Figure 20: Ozone, NO_y and NO in Arosa (ar), ozone at Jungfraujoch (jfj) and Taenikon (tae) during the exceptional case of an inversion reaching above the measurement site in Arosa.

Such exceptional events with an inversion layer localized between 2000 and 3000 are rather seldom. Indeed by comparing all the data available from winter and fall data during the campaign it turns out that only during 4 other days the upper limit of a fog layer at Säntis was localized at 2000 m or above. Despite the observation at Säntis even at these days Arosa was located above the inversion layer according to local meteorological measurements.

5.1.2.2 Inversion from 15th to 22nd of November 2001

The period from the 15th to the 22nd of November was characterized by high-pressure over central Europe. The centre of the high-pressure system was not exactly located over Switzerland; however it could keep frontal systems far away from Switzerland for the whole period. The sky at measurement stations located in northern alpine mountain region like Arosa (1840 m), Davos (1590 m), Weissfluhjoch (2690 m), Säntis (2490 m) and Jungfraujoch (3580 m) was clear or slightly covered by scattered clouds whereas in all the Swiss Plateau cities from Zürich (556 m), Bern (565 m), Basel (316 m), Lucerne (456 m), Neuchâtel (485 m), to St. Gallen (779 m) and in Chur (Rhine valley, 555 m) the sky was partly or strongly covered. Often these measurement stations reported fog. The temperature differences between Arosa and Chur > -1° (Table 10) clearly show that a strong temperature inversion decoupled both locations during day time (according to a moist adiabatic temperature lapse rate of 0.5-0.6°/0.1 km temperature differences around -7 and -9 are expected between Arosa and Chur in a non-stratified atmosphere). On the 16th, 17th, 19th and 21st the temperature values in Arosa were absolutely even higher than in Chur. Observations contained in the Alpine Weather Statistics about the development of the fog layer at Säntis (Table 10) and at Mount la Dôle (1670 m at the west end of the Swiss Plateau not far from Geneva) strongly suggests that the temperature inversion observed between Arosa and Chur describes a situation that is not only limited to the Rhine valley but is representatives for the entire Swiss Plateau (SMA, 1985). Figure 19

shows for ozone, CO and NO_y that their concentrations did not significantly change from the 15th to 22nd. The averaged concentrations of the measured primary pollutants during this time are much lower than the monthly mean (Table 11). Similar results were found for the VOC measurements (Li, 2003). On the other hand ozone shows an opposite behaviour: during this period its average concentration was about 13 ppb higher than the November mean of 36.3 ppb. The standard deviations of trace gas concentrations in the considered period are much smaller compared to the entire month. This is valid for all the measured trace gases (for ozone and CO the value are notably low, Table 11).

(ppb)	Mean 15 – 22.11.01		Nov mean	mean Nov/ mean	st. deviation 15 – 22.11.01		Nov st. dev
NO	0.07	<	0.23	3.3	0.14	<	0.52
NO_2	0.30	<	1.14	3.8	0.28	<	1.28
CO	136.5	<	166.0	1.2	9.7	<	49.3
Benzene	66.3	<	96.7	1.5	12.5	<	46.5
i-Pentane	33.0	<	82.8	2.5	14.6	<	57.4
Hexane	6.5	<	15.1	2.3	5.0	<	11.1
NO_y	0.74	<	2.00	2.7	0.46	<	1.70
O_3	46.3	>	36.3	0.8	1.7	<	9.7

Table 11: Trace gases concentrations measured from 15th to 22nd and comparison with monthly average (VOC - measurements provided by Li (2003)).

At the rather close measurement stations of Grabs and Vaduz (located below the inversion layer in the Rhine Valley) enhanced primary pollutants and lower ozone concentrations were observed during this period (Table 12). The result shows that the fresh emissions can be trapped below the inversion layer. The processes of titration with NO and deposition can lead to very low ozone concentration during such events.

	Mean 15 – 22.11.01		November mean
Grabs			
NO_2 [ppb]	16.2	>	12.9
O_3 [ppb]	1.7	<	7.4
Vaduz			
NO_2 [ppb]	17.0	>	14.6
PM10 [mg/m3]	35.7	>	24.7
O_3 [ppb]	2.7	<	8.8

Table 12: Ozone, NO_2 and PM10 concentrations at Grabs and Vaduz in the Rhine valley.

Similarly concentrations at different low altitude NABEL stations distributed on the Swiss plateau show the same behaviour as the 2 stations Grabs and Vaduz.

In Figure 21 a profile for O_3 and NO_x from the NABEL measurements in Duebendorf, Taenikon, Rigi, Chaumont, Davos, Arosa and Jungfraujoch (from bottom to top) was constructed for this inversion event. This analysis represents a qualitative result; which is quite plausible considering the meteorological stability that prevailed during these days. For comparison this profile was compared with the profile found during days in November and December 2001 when no inversion layer developed over the Swiss Plateau. A third profile was included for all days in November and December 2001 when a strong temperature inversion occurred (Figure 21). Forrer *et al.* (2000) reported an ozone profile made with NABEL measurements showing increasing ozone concentration with increasing altitude; however no distinction was made between inversion and no inversion events. The single event from the 15th to the 22nd shows for ozone and NO_x the strength of this inversion in the Figure 21.

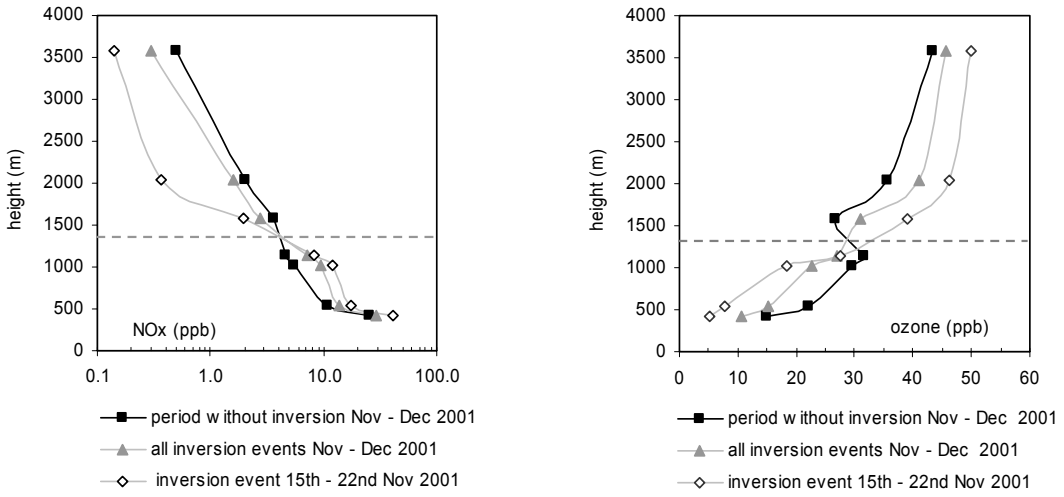


Figure 21: Vertical distribution of ozone and NO_x over the Swiss Plateau calculated for the period of inversion in November 2001 (red curve). For comparison are depicted days in November and December with temperature inversion (gray curve) and all days in November and December without temperature inversion (black curve). Stations are from bottom to top: Duebendorf (430 m), Taenikon (540 m), Rigi (1030 m), Chaumont (1140 m), Davos (1590 m), Arosa (2035 m) and Jungfraujoch (3580 m). To define days with and without inversion the temperature difference between Arosa and Chur was applied. Days with mean temperature difference above -4 °C during day time accounts for days with development of an inversion layer, whereas when the mean value is below -4°C no temperature inversion is expected (see also section 5.2 for explanation on this criterion).

Figure 21 shows the effect of strong inversion events. The three highest stations Davos, Arosa and Jungfraujoch show on average higher ozone concentrations during temperature inversion than during days where no temperature inversion is observed. For all the other stations from Dübendorf up to Chaumont the opposite behaviour is observed. Note however that the standard deviations calculated for the two cases “all inversion” and “without inversion” cover the differences observed at every location (Table 13). At Davos during no inversion events the ozone concentration was found to be clearly lower than at Chaumont and Rigi. To some extent this result can be explained by an enhanced exposure to ozone poor-air from the boundary layer of the Swiss Plateau during bad weather conditions in Davos (Chaumont is located in the Jura mountains N – NW of the Swiss Plateau, a front passage, e.g. which often come from N – NW possibly prevents the station from a too strong exposure to Swiss plateau boundary layer air). Another plausible explanation is an enhanced influence of very local emissions during bad weather periods which are in Davos higher than at Chaumont and Rigi (EMPA, 2000).

Ozone at Jungfraujoch shows a smaller difference between inversion- and no inversion events than Arosa (Figure 21) which provides evidence that the station of Arosa is more exposed to boundary layer influence and weather changes than Jungfraujoch. Dübendorf as well shows a clearly less pronounced difference between inversion- and no inversion days which could be explained by the proximity to strong emission sources reducing to some extent the influence of the synoptic weather.

The NO_x profiles (a logarithmic scale was used in order to better depict the influence on the three stations above the inversion layer, see also Table 13) show that in case of temperature inversion on average enhanced NO_x concentrations are found at station typically located below the inversion whereas slightly lower concentrations are

found on average in Davos, Arosa and Jungfraujoch. Despite the presence of an inversion layer it is surprising to see that the strong NO_x gradient for station located above the inversion. This is principally due to the relevance of local emission in Arosa and Davos.

Theoretically the point where the 2 lines cross each other represents the altitude reached from the inversion layer. In our case it seems plausible that the inversion layer was located between 1200 – 1500 m in these winter months. In early spring (February) the Chaumont (1140 m) was found to be sometimes located above and some times located below the inversion layer (Bronnimann and Neu, 1998). The fact that on average Chaumont showed lower ozone concentration during inversion could be explained by the fact that on these months stable inversion layers developed at higher altitudes than in early spring. The profiles of November and December are further discussed in section 5.2.2.

	Inversion events (N = 30)		No inversion events (N = 31)	
	O_3	NO_x	O_3	NO_x
Dübendorf	10.6 ± 9.5	29.1 ± 27.6	15.0 ± 11.6	25.1 ± 23.3
Taenikon	15.1 ± 10.0	13.8 ± 8.7	22.1 ± 11.1	10.8 ± 10.5
Rigi	22.6 ± 12.2	9.4 ± 7.1	29.5 ± 9.0	5.5 ± 5.6
Chaumont	26.9 ± 9.5	7.3 ± 5.1	31.6 ± 6.7	4.6 ± 3.4
Davos	31.0 ± 7.1	2.8 ± 2.9	26.7 ± 7.6	3.6 ± 3.0
Arosa	41.0 ± 5.7	1.6 ± 2.2	35.5 ± 5.9	2.0 ± 1.8
Jungfraujoch	45.6 ± 5.3	0.3 ± 0.8	43.4 ± 5.8	0.5 ± 0.9

Table 13: Vertical profiles of ozone and NO_x classified according to temperature difference between Arosa and Chur > -4°C (inversion regime) and < -4°C (no – inversion regime) for November and December 2001.

During the inversion event in November between the 15th and the 22nd the time series of ozone in Arosa and Jungfraujoch were very similar (see also Figure 21). Figure 22 shows the trace gas time series of NO_y at the two stations Arosa and Jungfraujoch during this strong temperature inversion event. During the event (delimited by the gray bars) there were some important discrepancies between the NO_y concentrations at both sites. Despite the lower concentration measured during this period the factor between the $NO_{y\ ar}$/ $NO_{y\ jfj}$ during the event amounted to 2.48 and did not differ from the same value calculated for the whole November 2001 (2.44). NO_y concentrations in the early morning on the 16th, 17th, 20th, 21st and 22nd was instead at both sites very similar. According to the weather types this occurred on days where subsidence was supposed to be strongest (Figure 22).

The NO_x/NO_y ratios were higher in Arosa and reflect the higher NO_x concentrations found in Arosa. A clear diurnal variation in Arosa was observed with a pronounced maximum during day time. The range of ratios found is 0.2 – 1.0. This ratio is typically about 0.1 – 0.2 in the free troposphere during spring time (Carpenter et al., 2000). During summer conditions a value of 0.3 - 0.4 is reported as a threshold to separate aged air from air with recent emission at rural places in the boundary layer (Olszyna et al., 1994).

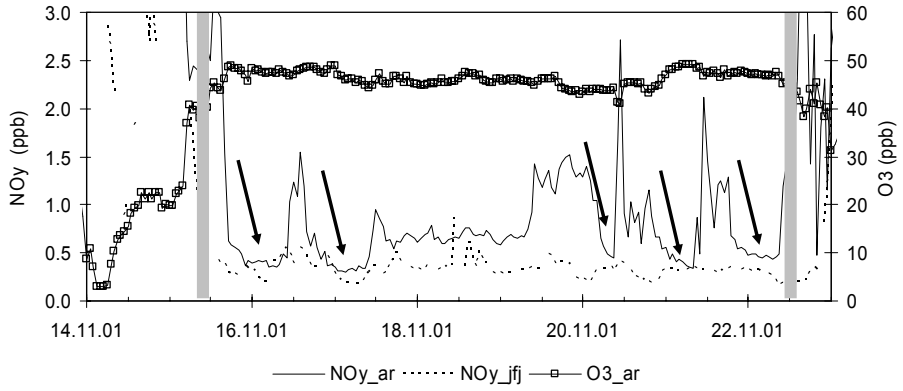


Figure 22: NO_y concentration in Arosa and Jungfraujoch between the 15th and the 22nd of November 2001 (ar = Arosa, jfj = Jungfraujoch) and ozone concentration in Arosa. Arrows mark early morning periods which show very similar NO_y concentrations in Arosa and Jungfraujoch.

The high peaks at day time are due to fresh emissions. Because of the strong inversion these emissions should represent the contribution of the village of Arosa. At night the ratio dropped and reached the minimum after midnight. The values were clearly below 0.4 indicating that air reaching the measurement station had not been recently in contact with emission. Figure 22 and Figure 23 show that in special cases characterized by high pressure Arosa can be influenced by free tropospheric air at the end of the valley out flow phase.

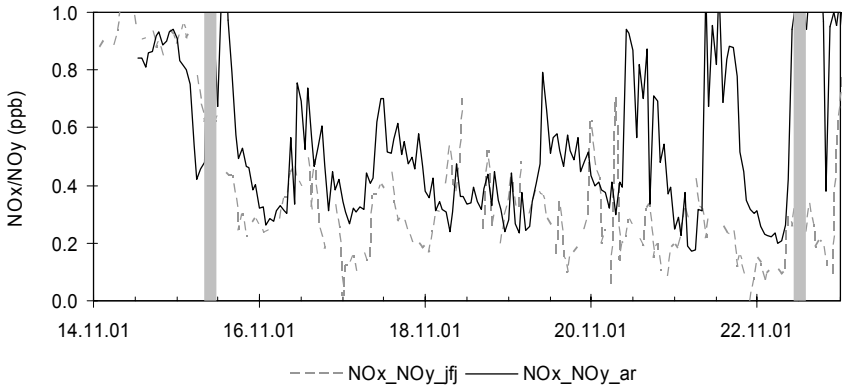


Figure 23: Ratio NO_x/NO_y in Arosa and Jungfraujoch between the 15th and the 22nd of November 2001 (ar = Arosa, jfj = Jungfraujoch).

5.1.3 Influence of fronts

In this section trace gas measurement in Arosa and other station during 3 situations characterized by a frontal passage are presented.

5.1.3.1 Front and North foehn of the 23rd of November 2001

The inversion layer described in section 5.1.2.2 was ended by the passage of a cold front approaching the Swiss plateau from NW direction. According to the Alpine Weather Statistics (SMA, 1985; Wanner *et al.* 1998) in the second half of the 22nd a cold front crossed the region of Zürich. The weather chart (Deutscher Wetterdienst) of the 23rd at 00 CET reports a cold front located over the central Alps.

The north foehn broke down in Arosa in the second half of the 23rd and was detectable by a strong change in relative humidity (from <30% to >90%), in wind speed (from 2-3 m/s up to 10 m/s) and in temperature (from 6° to -10°). The temperature difference between Arosa and Chur was strongly modified by this general change and Chur (Table 10). The evolution of the equivalent potential temperature (T_{ep}) in a NW to SE cross-section through Switzerland from Fahy (597 m) in the Jura to Locarno-Magadino (198 m) in Ticino gives an overview of the influence of this event on the lower troposphere over Switzerland (Figure 24).

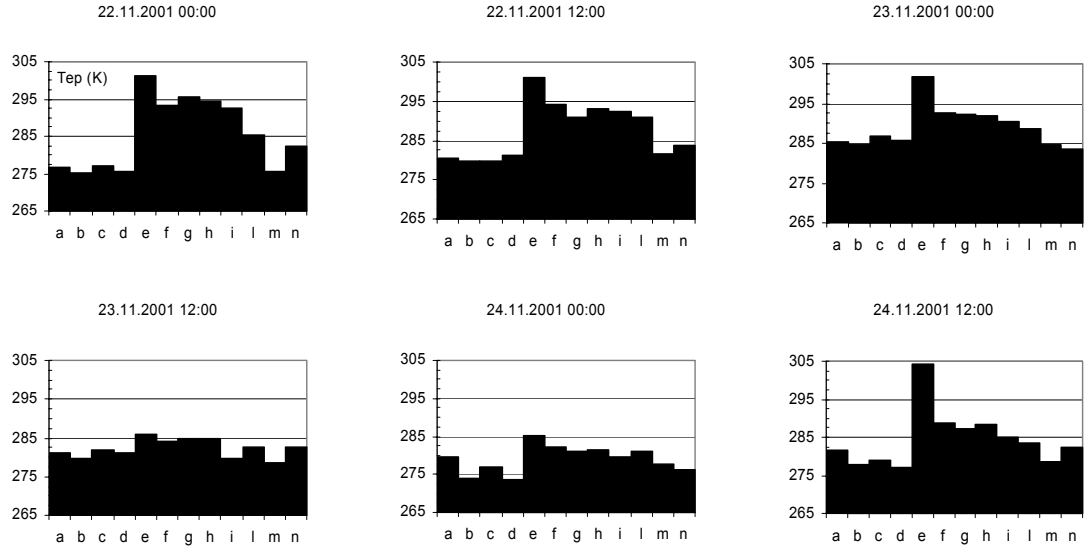


Figure 24: NW to SE cross-section through Switzerland of the equivalent potential temperature T_{ep} (K, calculated according to formula contained in Furger *et al.* 1989) derived from the following meteorological stations: a=Fahy (597 m), b=Wynau (416 m), c=Bern (567 m), d=Interlaken (578 m), e=Jungfraujoch (3576 m), f=Gütsch (2284 m), g=Pilatus (2105 m), h=Weissfluhjoch (2690 m), i=Arosa (2035 m), l=Davos (1590 m), m=Chur (555 m), n=Locarno-Magadino (198 m).

Initially at the time of the inversion layer the strong difference in T_{ep} between high mountain stations and low land stations shows the air mass stratification. The differences became less pronounced with the approaching of the pool of cold air associated with the front. On the 23rd at 00 CET only the Jungfraujoch was still sticking out of the cold air pool, whereas the similarity T_{ep} at stations north and south of the Alps suggests that this air had already crossed the Alps. About 12 hours later the all of Switzerland was covered by the same cold air mass advected behind the front. Late on the 24th a new (weak) inversion built up over the Swiss plateau.

Figure 25 (left) shows how ozone concentration decreased in Arosa and Jungfraujoch in the second half of the 22nd from about 50 ppb to about 35 ppb at 00 CET of the 23rd. Ozone at the low land station Payerne increased at the same time as a consequence of the definitive break up of the temperature inversion, the sharp decrease in CO concentration in Payerne beginning at 19 CET indicates the passage of the front.

The increase in ozone in Magadino south of the Alps is very sharp (Figure 25), is coincident with a strong decrease in NO_x concentration from 90 ppb to < 5 ppb (not shown). This sudden change indicates the arriving of the north foehn (at lower altitude). This trace gas behaviour was already studied in a climatology revealing that

on days with north foehn the yearly cycle of ozone in the boundary layer south of the Alps is very similar to the one found at Jungfraujoch (Weber & Prevot, 2002).

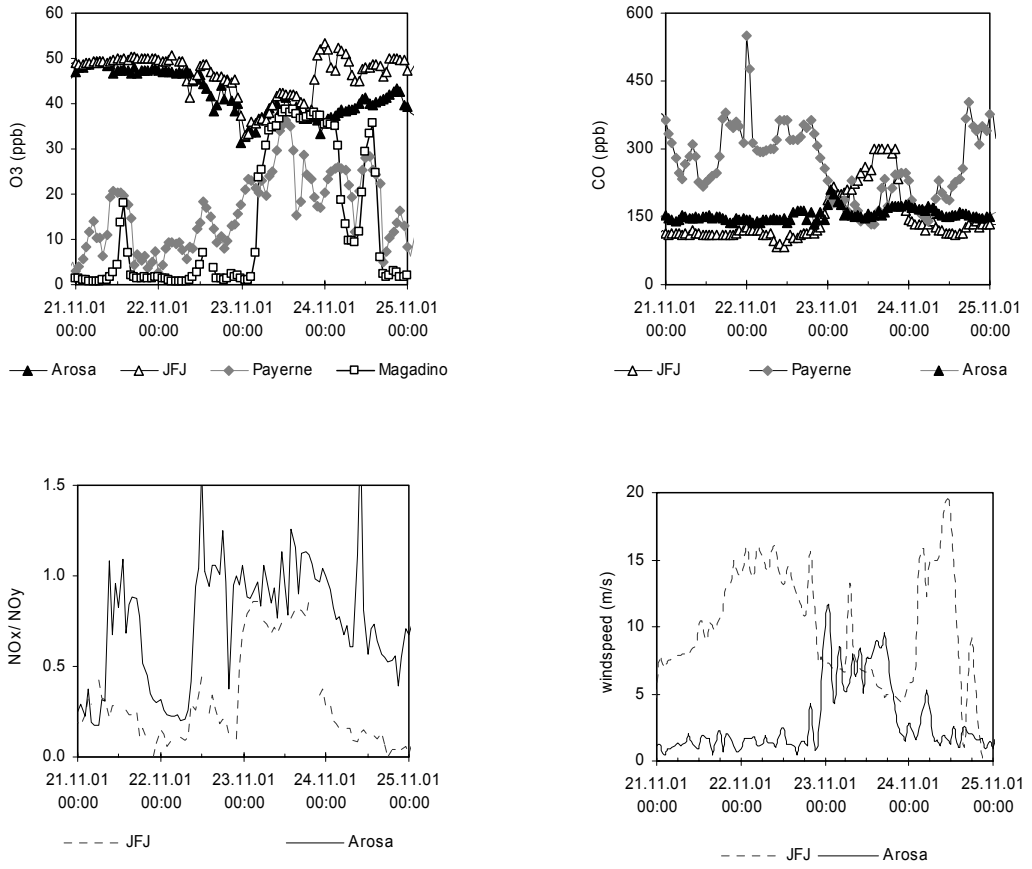


Figure 25: Chemical measurement in Arosa, Jungfraujoch (JFJ), Magadino and Payerne.

Compared with Payerne the change in ozone in Magadino begins few hours later, which is plausible considering the distance between both locations. Ozone concentration from 06 CET of the 23rd is very similar in each locations depicted in Figure 25. For Payerne this is a sign that relative clean and O_3 rich air advected behind the front has completely replaced air at low altitude from the former inversion. While CO concentration at Jungfraujoch reached very high concentration (only slightly lower than concentration measured in Payerne at the time of the inversion) the CO concentration in Arosa did not show any substantial increase and was about 150 ppb lower than at Jungfraujoch. Only at the presumed time of the front passage CO concentration in Arosa shows a peak (~200 ppb). The median value of CO at Jungfraujoch in November 2001 amounting 114 ppb evidences the exceptional character of this event. The large discrepancy with Arosa is hardly to explain, possibly during certain transport situations the Jungfraujoch is more exposed to the pollutant emissions from the Swiss Plateau than Arosa. CO concentration at Jungfraujoch collapsed within few hours from >300 ppb to <150 ppb shortly after 00 CET of the 24th. This occurred simultaneously with an ozone increase from < 40 ppb to >50 ppb. This information together with the strong decrease in the ratio NO_x/NO_y and the increase in wind speed from about 6 m/s to more than 15 m/s suggests that the Jungfraujoch was suddenly exposed to a new air mass. The ozone decrease in

Arosa and Jungfraujoch from the end of the 22nd can be attributed to uplifting of boundary layer air strongly subjected to titration and deposition. The NO_x/NO_y value close to the unit suggests that air arriving at both stations were recently in contact with fresh emissions, the air lifted up by the front passage. In the case presented here the cold front was followed by a north foehn. In this situation it is difficult to distinguish between the influence of the front and the influence of the north foehn. The next case describes an event in which the front was not immediately accompanied by a strong north foehn.

5.1.3.2 Front on the 27th of November 2001

According to the Alpine Weather statistic a cold front passed through the Swiss Plateau from NW direction in the morning of the 27th (indifferent weather) breaking up a weak temperature inversion located over the Swiss Plateau. Chemical measurement in Arosa and Jungfraujoch clearly denoted a strong ozone decrease in the afternoon of the 27th which was accompanied in both case by a strong increase in primary pollutant CO and NO_2 (Figure 26). The case of Arosa particularly illustrates the sequence of events on this day. At night high ozone concentration and low pollutants concentrations were observed in Arosa, in the morning more and more fresh emission from the village reached the station as it can be seen from the NO increase. In the afternoon NO concentration dropped to low values whereas NO_2 and CO concentration increased again at 15 CET. Obviously this second peak was not caused by emissions from the village. The strong increase in ozone in Chur indicates that the front had reached the inner Rhine Valley. The comparable ozone concentration in Arosa and in Chur together with the strong decrease in temperature difference between the same two locations shows that the atmosphere stratification during the inversion was definitely disappeared (about -3°C at midday, about -9°C at the end of the day). At midday on the 28th the ozone concentration in Arosa was similar as before the front passage. In contrast the temperature difference (-6°C) was at midday of the 28th still lower than before the occurrence of the front. On this event the strong ozone decrease was caused by ozone-poor air lifted up to the high alpine stations from the low boundary layer region.

During upward transport boundary layer air is diluted with air located at higher level. The dilution factor DF was estimated by following equation (from Zellweger *et al.,* 2000):

E 1
$$DF = \frac{[O_3]_{bf} - [O_3]_{bl}}{[O_3]_{bf} - [O_3]_{df}}$$

where $[O_3]_{bf}$ is the ozone concentration at the mountain station by undisturbed conditions, i.e. before the front passage. $[O_3]_{bl}$ is the ozone concentration in the boundary layer before the front passage and $[O_3]_{df}$ is the ozone concentration during the period influenced by the front passage in Arosa.

According to the ozone concentrations in Arosa and Chur before and during the front passage (00 to 15 CET on the 27th and 16 to 00 CET on the 28th) the estimated dilution factor amounts to 2.5-3 for the air lifted up from Chur to Arosa. NO_x compounds were also diluted during the transport. Considering the mean value of 3 ppb NO_x measured in Arosa in the period influenced by the front this imply a mean concentration of 7.5 – 9 ppb in the region of the Rhine Valley if loss processes are neglected during the up transport. At the location Grabs and Vaduz in the Rhine Valley on the 27th (between 00 and 15 CET) mean NO_x concentrations of 13.5 ppb

and 10.8 ppb were found which qualitatively well agree with our calculation. The difference could be attributed to dry and wet deposition (using average value about 3.9 ppb corresponding to about ~ 30% of the averaged NO_x concentration present in Grabs and Vaduz). Ozone concentrations in Arosa and Jungfraujoch were mainly determined by a different balance in titration processes within the air transported to the stations as it can be also figure out by the strong negative correlation between CO and O_3 (Arosa: R^2=0.81, JFJ: R^2=0.85) and between NO_y and O_3 (Arosa: R^2=0.61, JFJ: R^2=0.88) in the period from the 27th at 15 CET to the 28th at 12 CET.

On the time of this front passage ozone concentration at Magadino south of the Alps remained at low level all the time (< 3 ppb, not shown). This observation suggests that in the case described in the previous section 5.1.3.1 basically the north foehn was responsible for the substantial change in ozone and NO_x concentration and not the front itself.

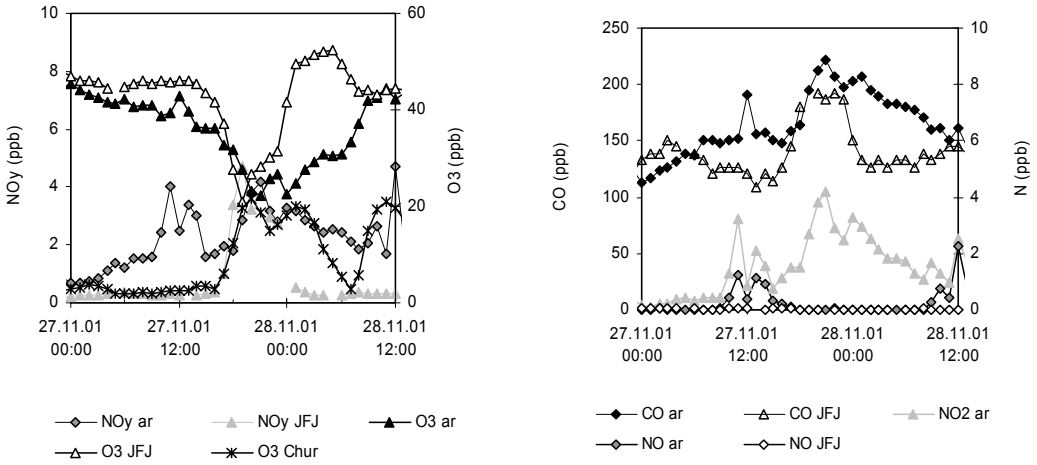


Figure 26: Trace gas concentration in Arosa (ar), Chur and Jungfraujoch during the cold front passage of the 27th of November.

5.1.4 The case of 12th -15th of November 2001

5.1.4.1 Chemical measurement in Arosa Davos and Jungfraujoch

Between the 12th and the 15th November 2001 a case occurred which was similar to the one we described above. At this time however much higher concentrations typical for the polluted planetary boundary layer close to densely populated cities were measured. Such high concentrations are not expected to be observed at remote stations (Figure 27). A simple calculation (assuming only road traffic sources) provides evidence that local emission alone was not responsible for the high concentration measured in Arosa. Assuming that:

- the maximum observed NO_y concentration during the night between the 12th and the 13th (12.3 ppb as a hour average) is composed by NO (20%) and NO_2 (80%), which is the case for very strong polluted air masses,
- a pool of cold air (inversion) measuring 0.5 ± 0.1 km^3 forms in the Arosa basin reaching the station and exposing it to the village emissions which are supposed to mix completely,
- 100 cars are at the same time moving in the Arosa area with a vehicle speed of 50 km/h and an emission factor (EM) of 1053 mg NOx/km (John *et al.*; 1999)

it was found that every of the 100 car need to drive 95 km in order to reach NO_y concentration measured during this event which is rather unrealistic.

Measurements in Arosa showed twice a very sharp increase in NO_y and CO concentrations which stayed during several hours at very high levels (Figure 27). Between the two consecutive peaks NO_y and CO concentration strongly decreased. It is however remarkable that the concentrations were still very high compared to the monthly median values (Table 9). O_3 measured at the LKO observatory in the village was completely depleted (values in Arosa Tschuggen were deleted by Meteo Swiss because they were believed to be unrealistically low). Both measurements in Arosa Tschuggen and Arosa LKO show a good correlation (November 2001 R^2=0.7) whereby O_3 data in Arosa LKO were usually somewhat lower than in Arosa Tschuggen ($O_{3\ Tschug}$=0.7*$O_{3\ LKO}$ + 15.3). It is therefore plausible that O_3 concentration at Tschuggen also dropped considerably but it is not certain that O_3 at Tschuggen was also completely depleted.

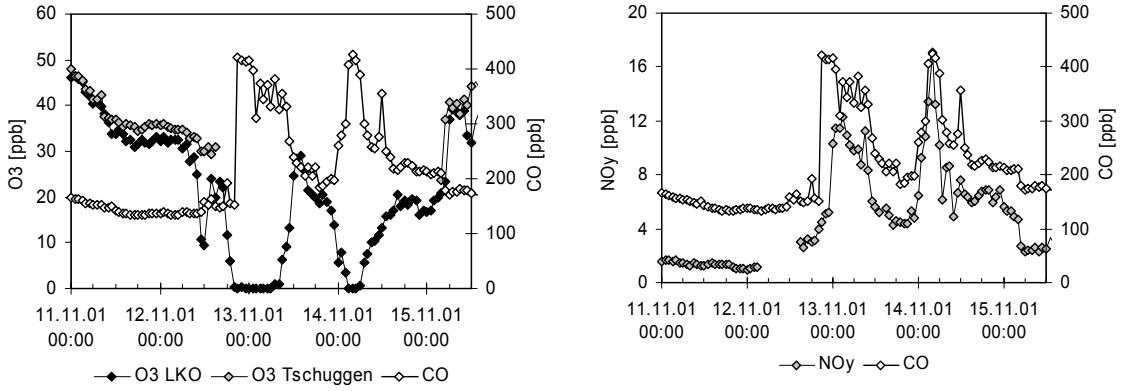


Figure 27: Time series of NO_y, CO and O_3* in Arosa between the 11th and the 16th of November 2001 (* measurement in the 150 m down slope located Observatory LKO, hourly average).

Measurements in Davos and Jungfraujoch provide further evidence that trace gas concentrations on these days was the result of a large scale event. In Davos both the drop in O_3 concentration and the increase in NO_x were simultaneous with the change described in Arosa. In particularly O_3 dropped below 2 ppb for 15.5 hours (Figure 28).

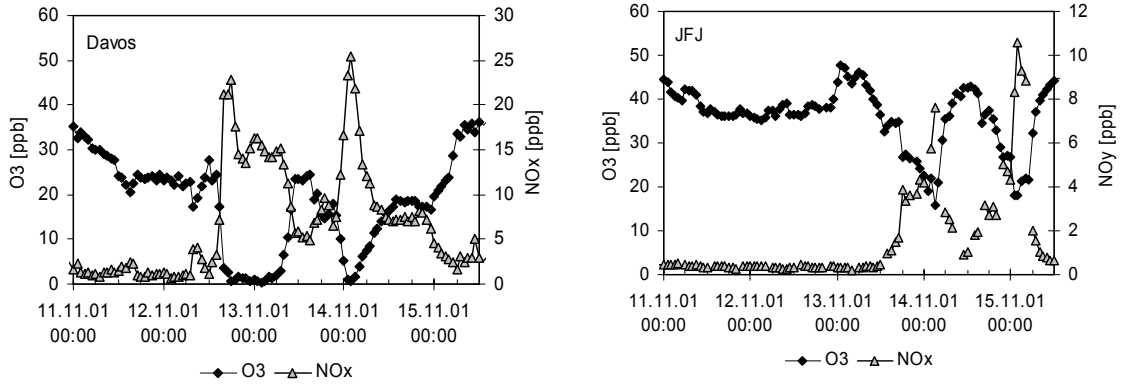


Figure 28: Time series of NO_x and O_3 in Davos and NO_y and O_3 at Jungfraujoch between the 11th and the 16th of November 2001 (hourly average).

A similar behaviour with pronounced peaks on two consecutive nights was observed at Jungfraujoch however with a time shift of about 24 hours, i.e. at the time of the first sharp change in Arosa and Davos nothing remarkable occurred at Jungfraujoch. Further minima (O_3) and maxima (CO, NO_y and NO_x) were less pronounced as in Davos or in Arosa. Table 14 provides a summary of this event. The grey area highlights the occurrence of the minimum (O_3) and the maximum (NO_y and CO).

	Night 12th – 13th Nov			Night 13th – 14th Nov			Night 14th – 15th Nov			Monthly median		
	NO_y (ppb)	O_3 (ppb)	CO (ppb)	NO_y (ppb)	O_3 (ppb)	CO (ppb)	NO_y (ppb)	O_3 (ppb)	CO (ppb)	NO_y (ppb)	O_3 (ppb)	CO (ppb)
Davos	22.8*	0.5	-	25.5*	0.8	-	7.9*	23.0	-	2.2*	29.3	-
Arosa	12.3	0[a]	422	17.1	0[a]	426	6.8	16.7	209	1.2	37.7	153
JFJ	0.3	47.1	120	7.7	15.7	253	10.6	18.1	289	0.4	44.7	114

Table 14: Minimum (O_3) and maximum (NO_y, CO) in Davos (* NO_x), Arosa ([a] LKO) and Jungfraujoch (hourly average)

While start of the event is shifted at Jungfraujoch, the recover from the disturbance at the three sites took place almost at the same time during the second part of the 15th.

5.1.4.2 Measurement at low land stations

During this event ozone concentration at several measurement stations located in the Swiss plateau and in the Rhine Valley was close to 0 ppb and was negative correlated with the NO_x concentration (Figure 29). Beside Payerne, Chur, Grabs and Vaduz also Taenikon and Duebendorf show the same variation in trace gas (not reported). In the Rhine valley the period with extremely low ozone concentration was longer than at stations of the Swiss Plateau region covering the entire period from the 12th to the beginning of the 14th. As it is shown for Payerne and Chur low ozone concentrations were mainly associated with weak wind.

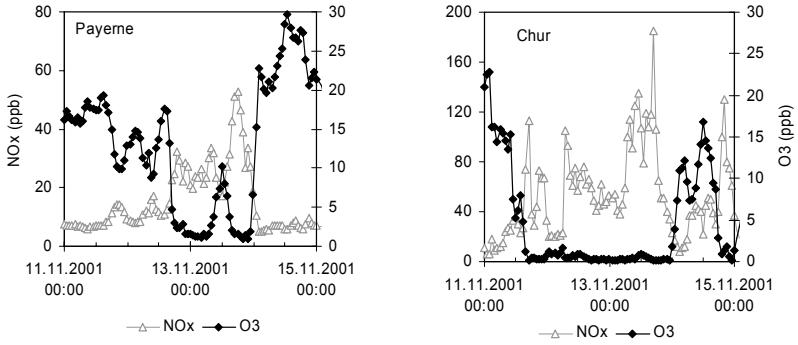


Figure 29: see legend next page.

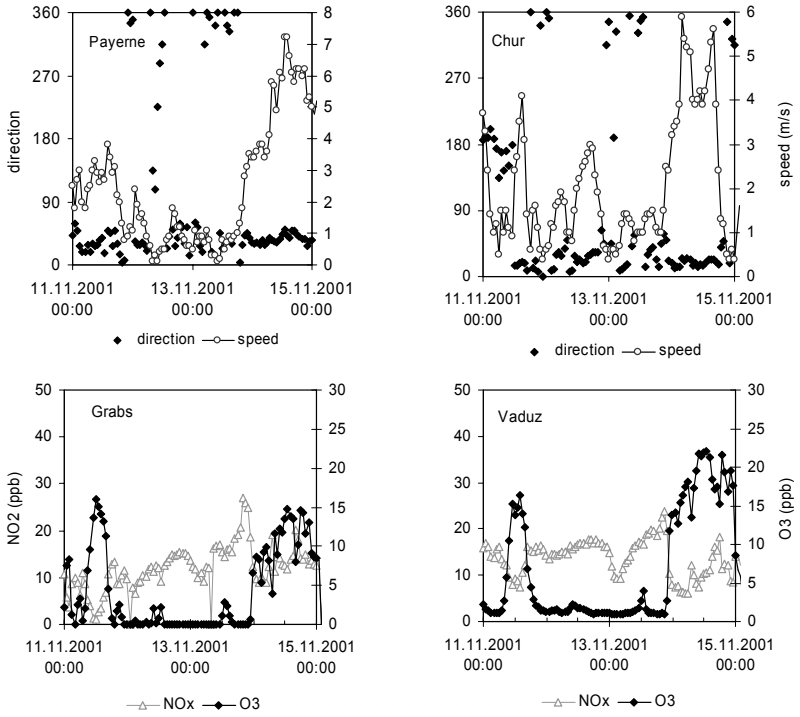


Figure 29: Ozone and NO_x measurements at the stations of Payerne Chur RhB, Grabs and Vaduz and wind at Payerne and Chur.

5.1.4.3 Meteorological situation

From the analysis of weather charts, meteorological sounding and information from the weather type of the Alpine Weather statistics it turned out that the meteorological situation both in a synoptic and local scale was rather complex. Between the 11th and the 15th a frontal passage was registered. Figure 30 shows that the pool of cold air arrived over Switzerland in the late afternoon of the 13th. The second O_3 drop in Arosa and Davos and the first ozone drop at Jungfraujoch can be therefore be attributed to the synoptical lifting of ozone poor air from the boundary layer as described for the previous case in section 5.1.3.2. The abrupt change in ozone concentration together with the wind speed increase at the beginning of the 14th at all low land stations indicates the passage of the front (Figure 29).

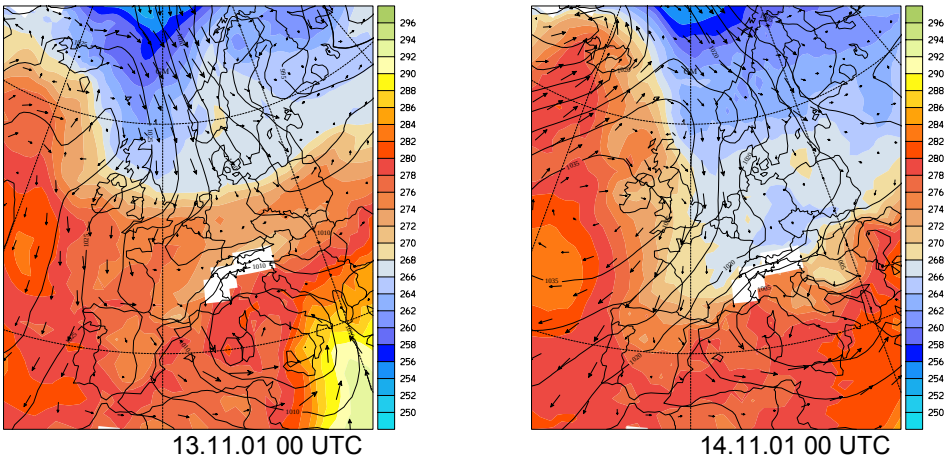


Figure 30: Temperature and wind at 850 hPa, sea pressure level based data from ECMWF fields indicate the arrival of the cold front at the end of the 13th of November 2001.

Before the frontal passage a strong inversion layer was located at about 1200 m over the Swiss plateau. A weak wind coming from SE direction was registered above the inversion up to 5000 – 6000 m. A change in wind direction from SE to NE above the inversion took place in the first half of the 12th. The inversion had completely disappeared at the end of the 12th, i.e at the time of the first ozone drop in Arosa and Davos. The meteorological sounding shows on the 13th cold air masses advected from N - NE direction together with a substantial increase in wind speed which took place at altitude <1000 m. At this time the front mentioned above crossed the Swiss Plateau leading to the second disturbance in Arosa and Davos and the first disturbance at Jungfraujoch. On the 14th strong winds still came up to 3000 m from NE whereas above 3000 m a much weaker wind was coming from S – SW direction. The change in wind direction at high altitude from N-NE to S-SW is mainly to be attributed to the influence of a low over Spain clearly recognisable in the 500 hPa chart. From the beginning of the 15th a new strong temperature inversion begun to develop over the Swiss Plateau as a consequence of a high pressure system over the Atlantic becoming more and more important. Weak wind turning from S to E-SE were observed above the inversion layer. This information gained from Payerne sounding (Meteo Swiss) fits qualitatively to the wind pattern at Jungfraujoch and Weissfluhjoch (Figure 31). At the time of the first peak in Arosa and Davos a change in wind direction from S to N had just taken place at Weissfluhjoch. The second peak at Jungfraujoch occurred after the change in wind direction from N-NE to S-SW and suggests that air lifted up by the front and further transported southward could have been advected back. Local wind measurement at Davos most of the time was similar as in Weissfluhjoch while Arosa indicate that the site was characterised by a calm (Figure 31).

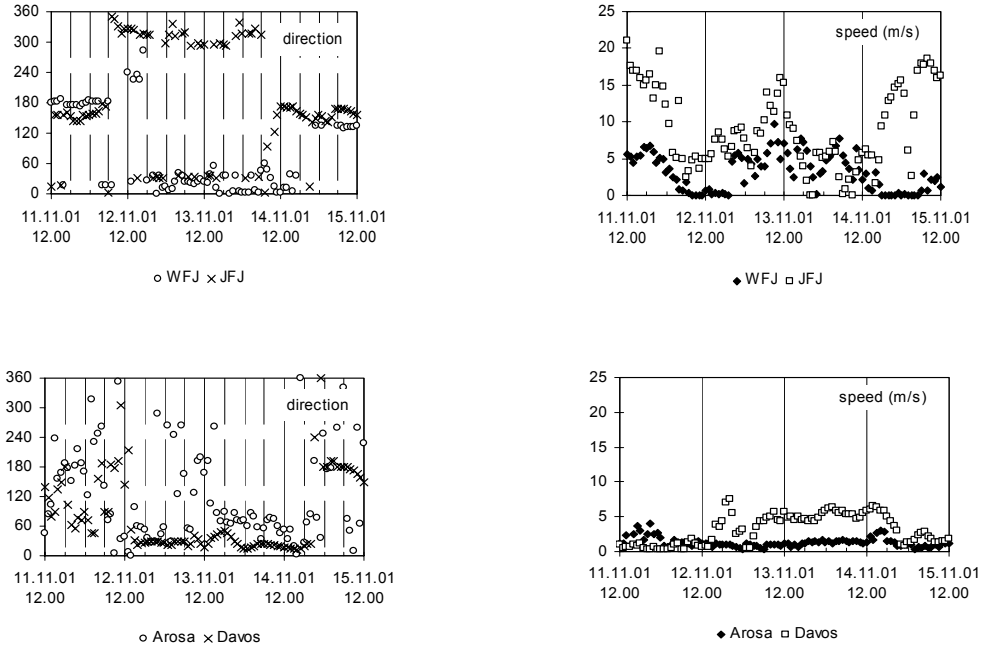


Figure 31: Time series of local wind at Jungfraujoch (JFJ), Weissfluhjoch (WFJ), Arosa and Davos.

5.1.4.4 Trajectories at Davos and Jungfraujoch

Backward trajectories (LM-Model) for the time period covering this event were available for Davos (Figure 32) and Jungfraujoch (Figure 33).

Backward trajectories reaching Davos came generally from the South until the 12th of November at 18 UTC at the time of the first drop in Davos (and Arosa). On the 11th 00 UTC trajectories never exceed the 800 hPa and high O_3 concentration of 35 ppb (November 2001 median 29.3 ppb) was measured at Davos (Figure 32). The ozone decrease of 10 ppb until the 12th at 18 UTC took place while trajectories come fast from the maritime boundary passing the Po basin at altitude mainly above 800 hPa (about 1700 – 1800 m above the surface). Only trajectories arriving at Davos on the 12th at 00 UTC stay 12 h at altitude below 800 hPa never exceeding however 850 hPa. 850 hPa was suggested by Forrer *et al* (2000) to represent the upper limit of the polluted boundary layer.

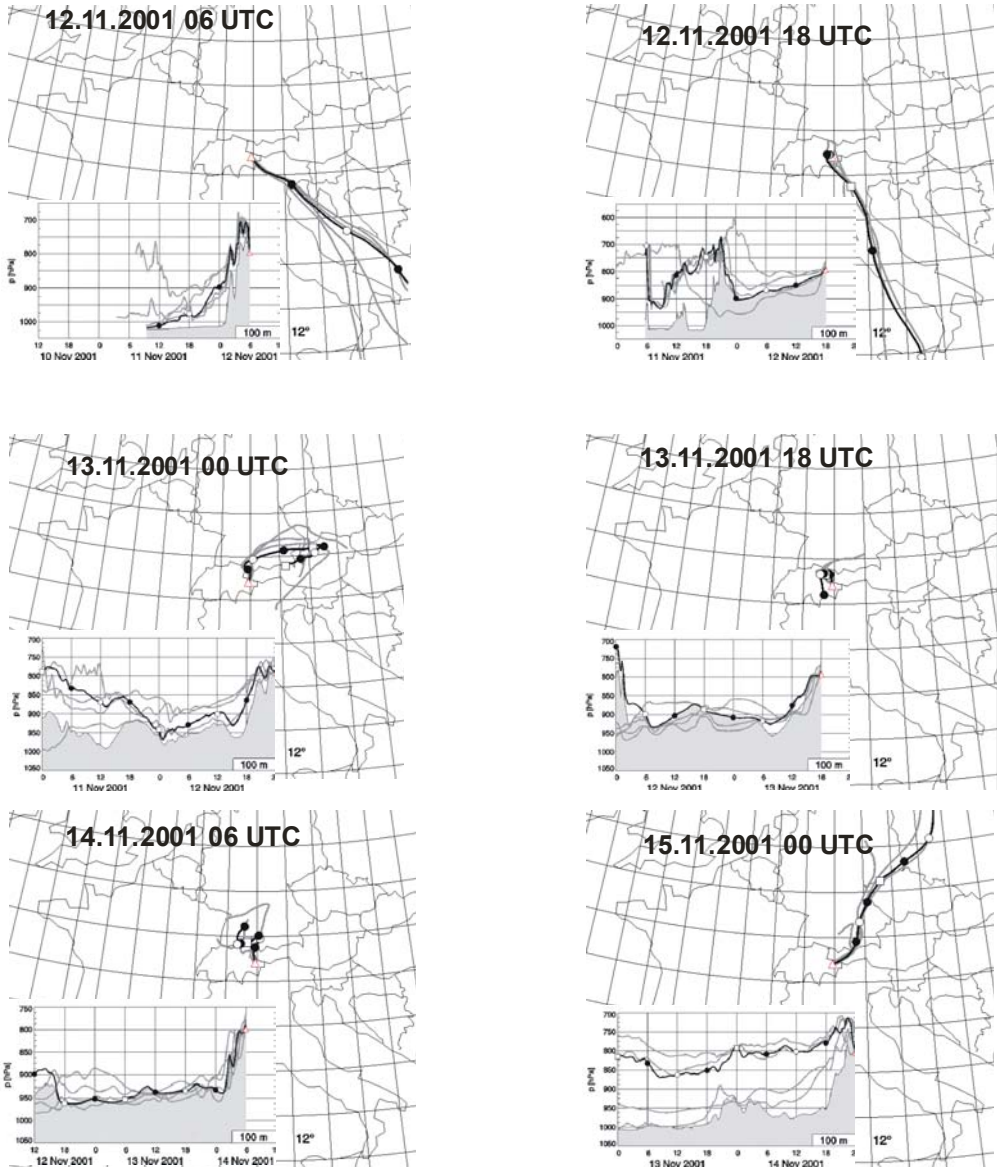


Figure 32: Backward trajectories arriving in Davos based on the Local Model (Meteo Swiss).

At the time of the first ozone drop in Davos trajectories during the last 18 hours almost don't move showing a very slow air motion up from the Rhine valley at altitude close to the surface. Except the last 18 hours the trajectories show a similar behaviour as the trajectories arrived before in Davos: rather fast transport at 800 hPa over the continent with following descent in the maritime boundary layer. The flow pattern suggests that air parcels were directly in contact with emissions from the Rhine valley for several hours. The strong temperature inversion present until the 12th has probably further supported ozone titration. Similar ozone and NO_x concentration in Grabs and Vaduz in the Rhine valley on the 12th and in Davos suggest that air from the Rhine valley reached almost undiluted the station of Davos. It is surprising that there is no synoptical evidence for this motion such a front passage. Exactly at the time of the ozone drop wind in Davos clearly turned to N-NE and increased in speed indicating that air was suddenly advected from the mouth of the valley (Rhine Valley) leading up to Davos

A very sharp drop in temperature between 16 and 20 in Davos (ΔT ~6 °), which is high for a covered and wet day as the 12th can possibly be regarded as the meteorological signature of the transport of cold air from the Rhine valley. The following trajectories from the 13th come from the NE at first and from the N later on consistently with the change in wind direction observed at Weissfluhjoch. All these trajectories suggest that air parcel were transported slowly and at very low altitude. At the time of the front passage in the late afternoon of the 13th and during the following night trajectories suggests the advection of air which stayed several hours at low altitude in an area including Rhine valley, the Swiss Plateau and South Germany. It is only from the 15th at 00 UTC that trajectories clearly come from a layer above 800 hPa. At this time O_3 concentration increases again and completely recovered in Davos.

The trajectories at Jungfraujoch are at first similar to the trajectories in Davos. They come from the south and travel fast over the Po basin at a rather high altitude. On the 12th at 20 UTC and on the 13th at 00 and 04 UTC trajectories came from altitude < 850 hPa and don't show the same pattern as in Davos: in particular no evidence of air moving slowly up to the mountain from a very close polluted region can be observed.

It is only from the late afternoon of the 13th, i.e. at the time of the front passage and decreasing ozone concentration at Jungfraujoch, that trajectories clearly showed substantial higher residence time over the Swiss plateau area. Particularly the trajectories arriving at 00 UTC on the 14th remain 48 hours at lower altitude over the Swiss Plateau. The trajectories are very similar to those described for Davos. Shortly after the passage of the front (14th at 04 UTC) trajectories suggest that air parcels were travelling fast over the entire continent. This flow pattern could be interpreted as cold air advected behind the front. A comparison with Davos (14th 06 UTC in Figure 32) shows a large difference in the flow pattern after the passage of the front. In Davos trajectories suggest an air mass motion from higher latitude only from the 14th at 12 UTC. It is interesting to note that while the ozone concentration at Jungfraujoch almost completely recovered after the first drop ozone concentration in Davos only partly increase, which is consistent with the flow pattern. At the time when the second disturbance reached the Jungfraujoch trajectories show a complete different pattern than during the first peak (from 15th at 00). They came from E-SE direction to the station after having moved at high altitude, hardly falling lower than 700 hPa. Trajectories arriving at 16 UTC shows an almost closed circulation over the Alps at

altitude >700 hPa indicating that air parcels were passing closed to the Jungfraujoch 30 h before. The trajectories are fully consistent with the change in wind direction at higher altitude described before and strongly suggest that 1. the second peak at Jungfraujoch was not caused by direct influence of the boundary layer and 2. air uplifted by the front in the course of the previous night have most probably caused the second peak at Jungfraujoch through a change in the circulation from northerly to southerly advection occurred at high altitude (2500 – 3000 m).

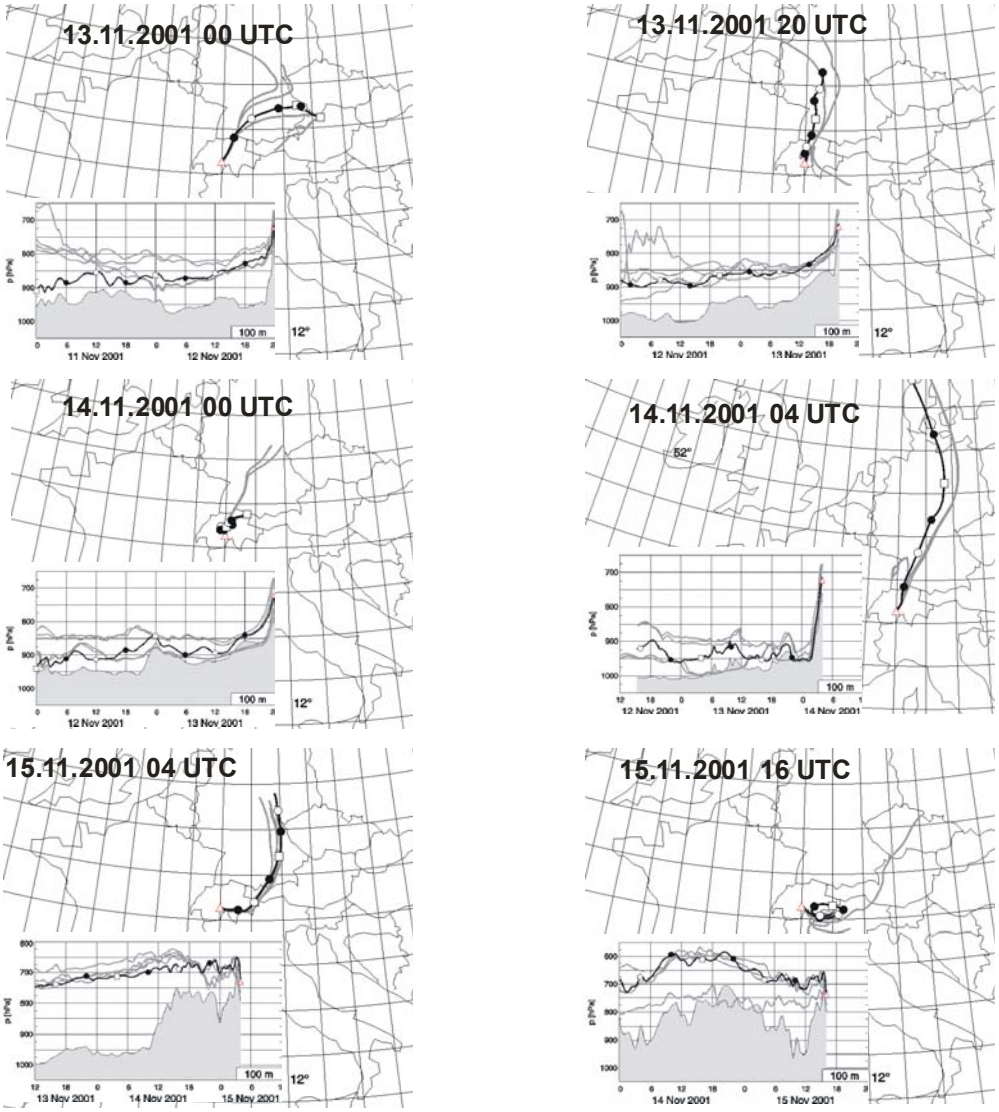


Figure 33: Backward trajectories arriving at Jungfraujoch based on the Local Model (Meteo Swiss).

According to trajectories arriving at Jungfraujoch on the 15th at 00 air parcel were located about 12 h before over the Swiss East Alps (in the region over Davos and Arosa). A comparison between the concentration at Jungfraujoch during the second disturbance and concentration in Arosa and Davos around noon (11-13 CET) is found in Table 15.

(ppb)	JFJ	Davos	Arosa
CO	260	-	294
NO_x	8.8	7.0	-
NO_y	9.4	-	7.0
O_3	19	16	15

Table 15: Comparison of concentration between pollution event during the night of the 15th at Jungfraujoch (maximum) and the mean value (average between 11 and 13 CET) observed in Arosa and Davos 12 hours before arrival at Jungfraujoch of backward trajectories.

This qualitative comparison suggests that only a very small dilution took place during the transport from the East Swiss Alp and Jungfraujoch. This could be further supported by a) the persistent high NO_y concentration and low O_3 concentration in Davos and in Arosa b) with the decreasing wind speed values on the Weissfluhjoch and c) the weak synoptic flow conditions prevailing over the Swiss Alps.

5.1.4.5 Conclusion remarks on the case 12th-15th November 2001

For the first peak at Davos at the end of the 12th no frontal passage occurred. Trajectories and the local wind measurement suggest for Davos a transport of air parcels from the floor of the Rhine valley. At this time ozone concentrations close to 0 ppb were measured at several stations in the Rhine valley as a consequence of a strong temperature inversion. The sharp change in the synoptic circulation from S to N advection might have triggered the first part of this event.

The second ozone drop at Davos and the first at Jungfraujoch were caused by the uplifting of ozone-poor air due to a cold front passage at the end of the 13th of November. Trajectories suggest slow advection of air which stayed several hours in a region included between the Rhine Valley, the Swiss Plateau and South Germany. This result suggests that such extreme ozone titration episodes are caused by regionally emitted pollutants reaching the high alpine site (~0-200 km). The second ozone drop at Jungfraujoch is not directly related to the passage of the front system but can likely be attributed to the disturbance occurred the day before. Ozone poor air from the boundary layer lifted on the 14th up to high altitude by the front passage was advected the day after towards the Jungfraujoch. This motion occurred at high altitude and only a weak dilution took place.

For Arosa no trajectories were available. Due to the close proximity to Davos it can be assumed that similar transport processes occurred in Arosa. At the time of the two ozone drops a weak but clearly NE directed wind was observed indicating advection from the direction of the mouth of the Plessur valley.

Analysing Jungfraujoch data from May 1993 to August 2002 it was found that during 295 h ozone concentration was <30 ppb. These periods were usually accompanied by high NO_x concentration (5.6±4.1 ppb). They mainly occurred in the cold season (November to March, 86% of the hours). These events during the cold season were distributed over 67 days. This corresponds to about 7-8 events a winter in which the ozone concentration is on average during 3-4 hours below 30 ppb. Zellweger et al. (2002) gives for undisturbed free tropospheric conditions seasonal mean NO_x concentrations ranging between 0.18 and 0.21 ppb. It is therefore plausible to attribute large part of these events to the uplifting of boundary layer air due to the passage of strong (cold) fronts. On the same time this shows the importance of such events for the export of pollutants from the boundary layer in to the lower free troposphere.

5.1.5 Comparison with CONTRACE field campaign

Frontal passages do not only induce a transport of pollutants to the high mountain peak, as it was shown in the fronts events presented above, but are also capable to carry up boundary layer air into the free troposphere (Bethan *et al.*, 1998; Purvis *et al.*, 2002). The time scale of this air motion ranges from 1 to 2 days for air uplifted ahead of approaching cold front up to the upper troposphere (Cotton *et al.*, 1995). Huntrieser *et al.* (2002) identified layers with enhanced pollutants concentration during the CONTRACE campaign (Convective Transport of trace Gases into the middle and Upper Troposphere over Europe, November 2001). These layer were attributed both to events of fast uplifting of fresh European emissions and to events of advection of aged North American emissions.

As the consequence of polluted Mediterranean air rapidly uplifted by the same frontal system described in the last section enhanced CO concentrations were measured during the flight campaign on the 14th of November at 3000 m altitude (~120 ppb) together with O_3 concentration between 30 and 40 ppb (Huntrieser, personal communication). CO concentrations on that day were however much lower than CO concentrations found at similar altitudes like Jungfraujoch (>200 ppb) and Arosa (> 400 ppb, Table 14). The comparison suggests the possible role of the Alps chain in intensifying the uplifting of pollutants from the boundary layer during such fronts events. Similar conclusion could be drawn by comparing O_3 concentrations. At Jungfraujoch the lowest O_3 concentrations were half of what measured at similar altitude during the flight.

During the front case of the 22nd and 23rd of November the flight over south Germany at an altitude between 2000 and 6000 m revealed CO concentrations between 120 and 150 ppb and NO_y concentration ranging between 1 and 6 ppb. (Huntrieser *et al*., 2002). CO concentrations at Jungfraujoch (up to 300 ppb) and Arosa (up to 200 ppb) measured during the frontal passage were once again clearly higher than CO concentrations registered during the flight. NO_y concentrations measured during the flights were higher than at the alpine stations (2.5-3 ppb). Possibly during uplifting in the mountain region NO_y was more subjected to dry and wet deposition along the slope than it was in the free atmosphere over the plain region. The comparison possibly suggests the intensifying effect of orography during strong fronts. The proximity of a strong source such as the Swiss plateau could emphasise the effect of the orography.

5.2 Influence of vertical stability in winter

5.2.1 Temperature and ozone difference between Arosa and Chur

Temperature difference between two measurement stations located at different altitudes can provide information about vertical stability of the lower troposphere. In the case study presented in section 5.1.2.2 one sees that the development of a stable temperature inversion in the middle of November 2001 could strongly influence trace gas concentrations in Arosa. In another case (section 5.1.3.2) the passage of a cold front in Arosa induced both a strong decrease in temperature and in ozone concentration. In these two cases the temperature difference between Chur (555 m) and Arosa (2035 m) was in relation with two different pollutants transport situations.

Figure 34 shows the relationship between the temperature difference ΔT(Arosa – Chur) and the ozone difference ΔO_3 (Arosa – Chur) calculated as daily averages between 10 and 16 CET. The highest slopes were obtained for the coldest months (November to January). Strong positive temperature differences between Arosa and Chur occur only during these cold months and were related to the development of strong temperature inversion. In February and March instead when the inversion regime slowly breaks down none of the days revealed a positive temperature difference ($\Delta T > 0$) and the slope of the correlation got lower. Temperature difference of about –8 °, suggesting the completely absence of air stratification in the lower atmosphere, occurred instead in every month shown.

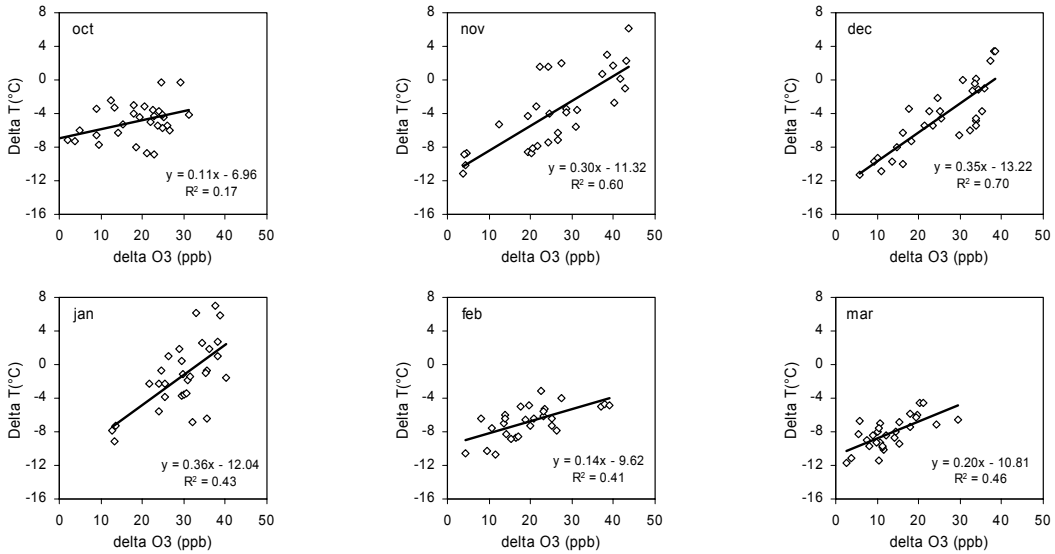


Figure 34: Temperature difference between Arosa (2035 m) and Chur (555 m), difference in ozone concentration between Arosa and Chur and their relationship. Hourly average between 10 and 16 CET were used, October 2001 – March 2002.

Information about front passages contained in the Alpine Weather Statistics (AWS) was combined to the previous analysis in the scope to better understand the influence of different meteorological situations on the relationship between ΔT and ΔO_3. In the AWS-record every front passage in Zurich is registered, attributed to one of the two time intervals 00–12 CET or 12–00 CET and eventually classified as “cold front”, “warm front” or “occlusion”. Passage of a front was not only considered relative to its registration time. A cold front passage was accounted for three consecutive time intervals (36 h) whereas the passage of the (weaker) warm front was only accounted for 2 consecutive time intervals (24 h). The same was done for occlusion events (24 h). Like this, not only the situation at the front passage itself was considered but also at the time immediately after (often periods with advective weather). Figure 35 shows for events influenced by fronts temperature difference between Arosa and Chur tended to be strongly negative and differences in ozone concentrations were low. A front passage breaking an inversion layer (often in winter time) reestablishes the typical temperature gradient of -0.5-0.6°/100 m which corresponds to a ΔT(Arosa – Chur) of about -9° and favor the vertical transport of ozone poor air from the boundary layer up to higher altitude. At low altitude air is replaced by “cleaner” air advected fast behind the frontal system which induces an increase in ozone on the plain (Figure 36, see also cases in section 5.1.3). Cold fronts influenced episodes were more frequent than those influenced by warm fronts

and they seem to act more strongly on the measurements in Arosa than warm fronts do. Figure 35 indicates that some points accounted as influenced by fronts show high values of temperature and/or ozone difference. An important reason for this observation is to find in the time resolution of the record of the fronts passages which is rather low. If a front crossed Zurich at the end of the time interval, it would probably not strongly influence the atmosphere above Chur and Arosa yet. Note that Zurich is located about 120 km in the NW direction compared to Arosa and Chur. A front registered in Zurich could even dissolve or lose its strength before arriving in the inner Rhine Valley without notably influencing measurements in Arosa. In addition the time with strong uplifting ahead the front is rather short (hours). After the front passage, ozone in Arosa might be restored more rapidly than the temperature difference. This could explain why, under influence of fronts, temperature difference between Arosa and Chur is low while the difference in ozone is already high (Figure 35, see also section 5.1.3.2).

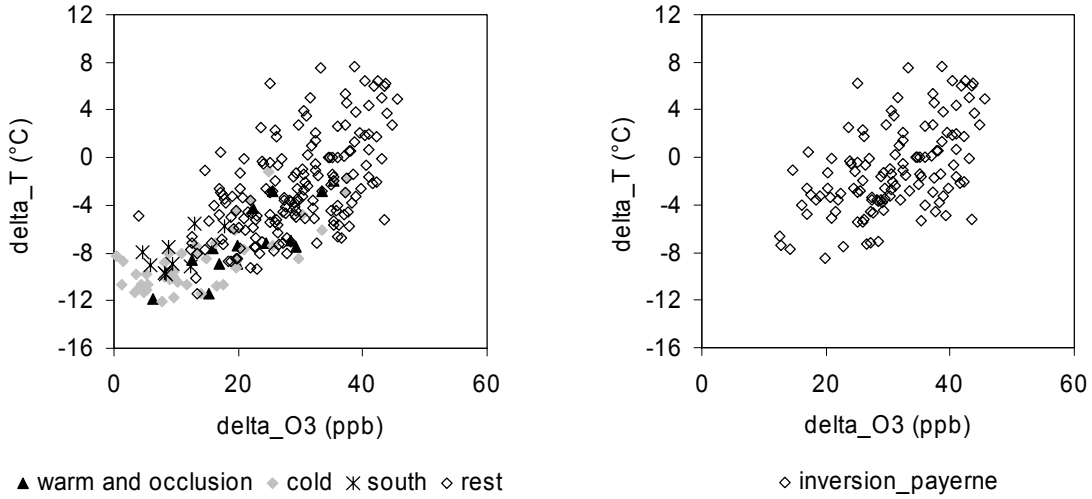


Figure 35: Left: temperature difference between Arosa (2035 m) and Chur (555 m) is positive correlated with difference in ozone between both locations, from November 2001 to February 2002 (R^2 = 0.52, each point means a 12 h interval). Warm and occlusion: periods influenced by warm front passage or occlusion. Cold: periods influenced by a cold front passage. South: periods influenced by south foehn. Rest: remaining fraction. Right: measurements in Arosa by an occurrence of an inversion layer in the Payerne sounding between 600 m and 2000 m (> 2°).

Figure 35 also shows how south foehn influenced the relationship between ΔT and ΔO3 in the same way as a front passage. The effect of a foehn on ozone concentrations in Arosa and Chur was however opposite (Figure 36). The effect of foehn will be discussed in more details in section 5.3. White points in Figure 35 (labelled as "rest") represent time intervals which were not accounted as influenced by south foehn or front passages. Many of the "rest" intervals represent periods characterized by inversion layer. Time intervals taken during the existence of a temperature inversion in the Payerne sounding (at 00 UTC and 12 UTC) between 600 m and 2000 m (which is the altitude of our investigation site in Arosa) also appear in Figure 35.

This result suggests that whenever a temperature difference between Arosa and Chur is found to be larger than about –4° an inversion layer is usually located above the Swiss Plateau. In this case not only Arosa and Chur are thermally decoupled.

Figure 36 shows the absolute values of ozone in Arosa and in Chur, relative humidity in Arosa and the frequency of the weather situations. At 31 days (out of 120 days considered) measurements in Arosa were influenced by a front passage whereas South foehn occurred about 4% of the time. From the remaining fraction about 75 % of the time there was an inversion layer located over the Swiss Plateau.

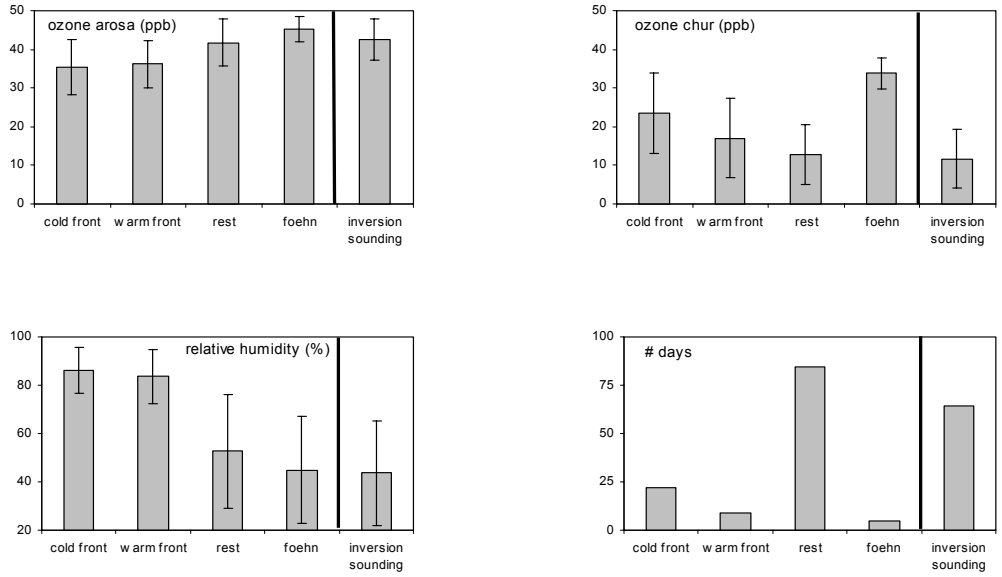


Figure 36: Ozone concentration in Arosa and Chur, relative humidity in Arosa and occurrence of meteorological situation described in the text. Cold front: periods influenced by a cold front passage. Warm front: periods influenced by warm front passage or occlusion. Foehn: periods influenced by south foehn. Rest: remaining fraction. Inversion sounding: inversion in the Payerne sounding.

A comparison between the synoptic weather classification according to Schüepp and the class “front”, “rest” and “inversion sounding” shows that the days influenced by a front passage mainly occurred during north advection (40%), west advection (17%), indifferent weather type (17%) and mixed weather (11%). Days in the category “rest” were mainly characterized by anticyclonic conditions (29%), indifferent conditions (26%) while north advection was found only in 10% of the time and west advection in 16%. For days in which an inversion layer was located over the Swiss Plateau the tendency found in “rest” was more pronounced. These days were characterized by anticyclonic weather (36%), indifferent conditions (28%), while the percentage of west advection (10%) and north advection (3%) further decreased.

This result indicates that the lowest ozone concentrations in Arosa were often found during unstable bad weather situation (such as advective weather connected with fronts) in which ozone poor air was advected from the boundary layer.

Backward trajectories for days characterized by influence of a front passage as previously described above originate almost exclusively from westerly and northerly directions (Figure 37). These trajectories travel usually fast over Europe (1.98 ± 0.95 day over Europe) and often exceed the 800 hPa level. Trajectories finally reach Arosa moving up from lower altitude. These trajectories indicate that air masses have been directly influenced by pollution sources at lower altitudes in the boundary layer.

Trajectories associated with situations of temperature inversion (over Switzerland) usually originate from higher altitudes and stay longer over the European continent (2.35 ± 1.38 day over Europe, Figure 38). In such situations mixing with fresh emissions causing ozone titration is less probable. Trajectories in Figure 38 indicate that some times air is transported down from higher altitude (700-500 hPa). Ozone climatology contained in Logan (1999) shows a small increase from about 40 to about 50 ppb between 700 hPa and 450 hPa (northern hemisphere, 30-60°N) in January. Higher ozone concentration associated with trajectories depicted in Figure 38 can also be related in some cases with transport of ozone rich air.

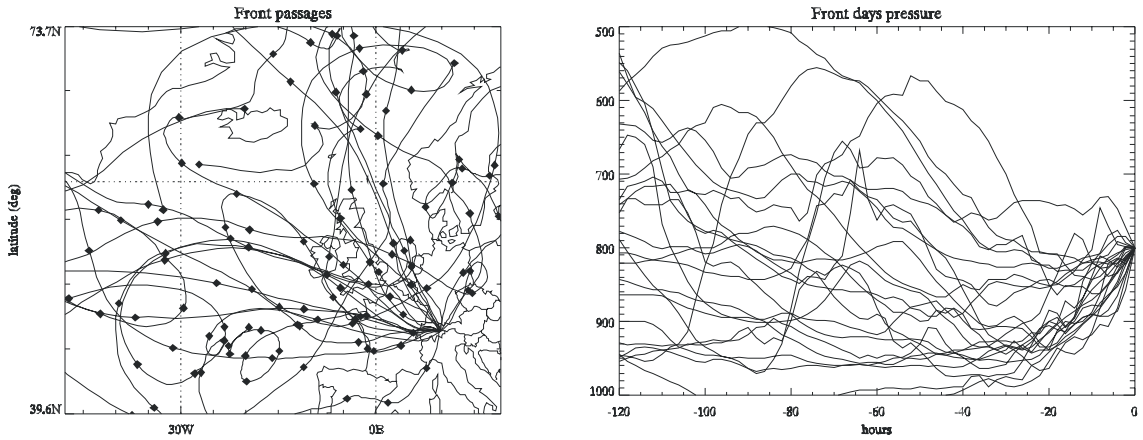


Figure 37: Backward trajectories arriving in Arosa at 06 UTC for the front cases (cold- warm – front and occlusion together, within the time interval 00–12 CET). Trajectories between November 2001 and February 2002 (for better understanding only half of the trajectories are plotted). Black marks are defined for a 24 h interval.

This accounts most of the time for the higher ozone concentrations associated with these events. However other reasons explaining high ozone concentration might not be excluded. One could argue that the origin of this enhanced ozone concentration in Arosa is connected with stratospheric intrusion. Using long term measurements of beryllium activity, ozone concentration and humidity it was found that stratospheric air masses can reach altitudes down to 3000 m (e.g. 28 stratospheric air injections at Zugspitze in January in 10 years) but rarely reach 1700 m (Elbern *et al.*, 1997). Therefore direct intrusions from the stratosphere are not important factors enhancing ozone concentration during inversion regime in Arosa. Nevertheless, in some case it is somehow plausible to think that, after intrusion in the free troposphere, aged stratospheric air masses can slowly subside and in a second moment reach lower altitude (Stohl *et al.* 2000). Bronnimann & Neu (1998) found for late winter - early spring at Chaumont (1140 m) that upon special conditions (inversion layer located below Chaumont, fair weather condition, simultaneous occurrence of low value of total ozone column (i.e. stratospheric ozone) and NO_x concentration ~3 – 3.5 ppb) the origin of high ozone during day time can already be attributed to local photochemical activity. Except for February where local photochemical activity already determine ozone in Arosa (see also 6.2), local photochemical activity is not expected to substantially contribute to the higher ozone concentration in Arosa during inversion events in winter. Another possible reason for high ozone concentration is given by Huntrieser *et al.* (2002) in the form of intercontinental transport and photochemical activity occurring on this scale. On the 19th of November 2001 (CONTRACE) air masses over Scandinavia at an altitude between 2 and 5 km were

found to be originated at lower altitude in the North American continent, from where they were uplifted by a strong frontal system 5 days before. The enhanced ozone concentrations (5-10 ppb, compared to a background profile) found in a layer with horizontal extension of more than 1000 km were attributed to photochemical oxidation of the uplifted pollutants during the transport from North America to Europe. Interestingly trajectories ending in Arosa on the 20th and 21st of November (inversion event described in section 5.1.2.2) show a rapid motion from the Scandinavia region (about 2 days over Europe on the 20th and about 1.74 days over Europe on the 21st). Air parcel were originating at an altitude of 600 - 750 hPa when they were over Northern Europe and Scandinavia. This suggests that enhanced ozone concentrations registered at Arosa on these two days (Figure 19 and Figure 20) could eventually be the results of photochemical oxidation of pollutants uplifted in North America. Li *et al.* (2003) postulated that oxidation of European emissions could lead to photochemical ozone production. The analysis compared ozone concentrations in Arosa with residence time of air parcels during days characterised by extremely strong inversions in November and in December and quantified an ozone increase in Arosa of about 1.3 ppb/days over Europe.

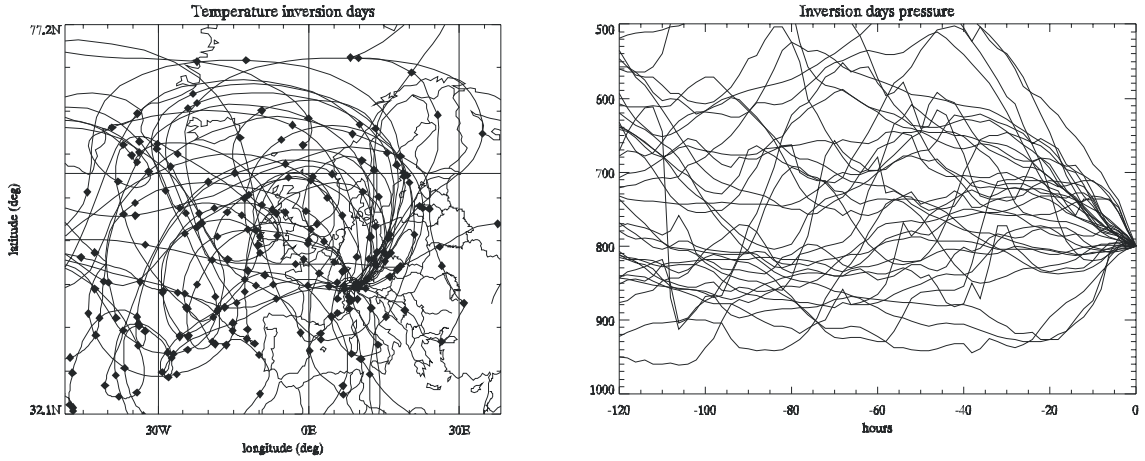


Figure 38: Backward trajectories arriving in Arosa for inversion cases (within the time interval 00 -12 CET), Trajectories between November 2001 and February 2002 (for better understanding only half of the trajectories are plotted). Black marks are defined for a 24 h interval. Inversion case includes case with temperature difference > -4° between Arosa and Chur.

5.2.2 Further remarks on November and December 2001 profiles

The use of different measurement stations distributed all over the Swiss Plateau and on the Alpine region confers to the averaged profiles depicted in Figure 21 a general validity for the relevant meteorological processes taking place in the lower troposphere in winter, namely inversion regime and advective weather. The averaged profiles are optimally in accordance with these two important meteorological phenomena. It is surprising that a rather simple criterion such as temperature difference between Arosa and Chur yields the observed separation of trace gas concentrations at every station considered. The success of the analysis is explained by the fact that temperature difference between these two stations is partially representative for a larger area how demonstrated the coupling with the Payerne sounding (Figure 35). The large standard deviation found point however to the complexity of results generalisation.

The representativity of ground-level measurements is frequently affected by local influences. For example the analysis of ozone measurements from more than 300 German stations revealed that the average radius of representativity was only 3-4 km (Tilmes & Zimmermann, 1998). The knowledge on the peculiarities of every single stations is however difficult. For example Bronnimann and Neu (1998) found that the measurement station Chaumont and Rigi were in some case located above strong inversion in early spring. Nevertheless these stations were not completely decoupled from the layer below the inversion. NO_x-rich air originating below the inversion could be clearly detected on the slope leading to the measurement stations. This suggests together with large values of standard deviation mentioned above that the image of temperature inversion acting as an absolute barrier against vertical air transport is to some extent only an ideal one.

The discrimination into days with and without inversions which is based on Figure 35 was newly performed. The criteria were set in order to select extreme events, i.e. extremely strong inversion events and days clearly characterised by no inversion (days were only considered as inversion if temperature difference between Arosa and Chur was > 0° and ozone difference between the same locations was > 30 ppb; days without inversion if the temperature difference was < -8° and ozone difference was < 10 ppb).

The November and December 2001 data set was therefore reduced (Table 16). Figure 39 depicts the profiles calculated according to the sharper criteria (termed as B in the figure) and compares them to those already depicted in Figure 21 (termed as A).

The trends already observed in Figure 21 are further strengthened. In particular it is evident that in case of very strong inversion the ozone concentrations in Arosa and at Jungfraujoch are very similar (Figure 39).

This trend is valid also for the profile “without inversion”, particularly steep is the ozone profile between Rigi and Jungfraujoch (excluding Davos). The B profile of NO_x for days “without inversion” show a mean NO_x concentration > 1 ppb at Jungfraujoch which is higher than NO_x concentration for disturbed free troposphere (0.6 ppb) given by Zellweger et al. (2002). This indicates that vertical transport of planetary boundary layer air was particularly efficient on these days and more marked than in the corresponding profile A. These days were probably rather strongly influenced by uplifting caused by front passages. The application of sharper criteria did not lead to a substantial reduction of the standard deviations in the 2 categories (compare Table 16 with Table 13).

Figure 39 also depicts the difference between inversion and no inversion cases for the averaged profiles. It is surprising to observe the symmetry of the curve of ozone relative to the 0 ppb – axis. Similar results are also found if masse is used (μg/m3) instead of mixing ratio (ppb). The calculation of the area below the curve of the μg/m3 yields to higher value above the inversion layer than below it (Figure 39 depicted the area only for the profile calculated with the sharper criteria). The profile of NO_x instead does no reveal a similar behaviour as the profile for ozone.

The first interesting point is that the alternation between inversion regime weather and no inversion regime weather affects in the ozone profiles a layer up to 3500-4000 and is therefore not restricted to lower altitude stations. This trend is clearly more pronounced for the extreme events. Also the magnitude of the change between the two regimes is similar below and above the inversion altitude. Zellweger *et al*. (2002) estimated that the Jungfraujoch in winter is about 32% of the time influenced

by the planetary boundary layer through south foehn events, front passages and strong frontal systems. The permanently undisturbed free troposphere is obviously located above the alpine crests. This is confirmed by the present profiles.

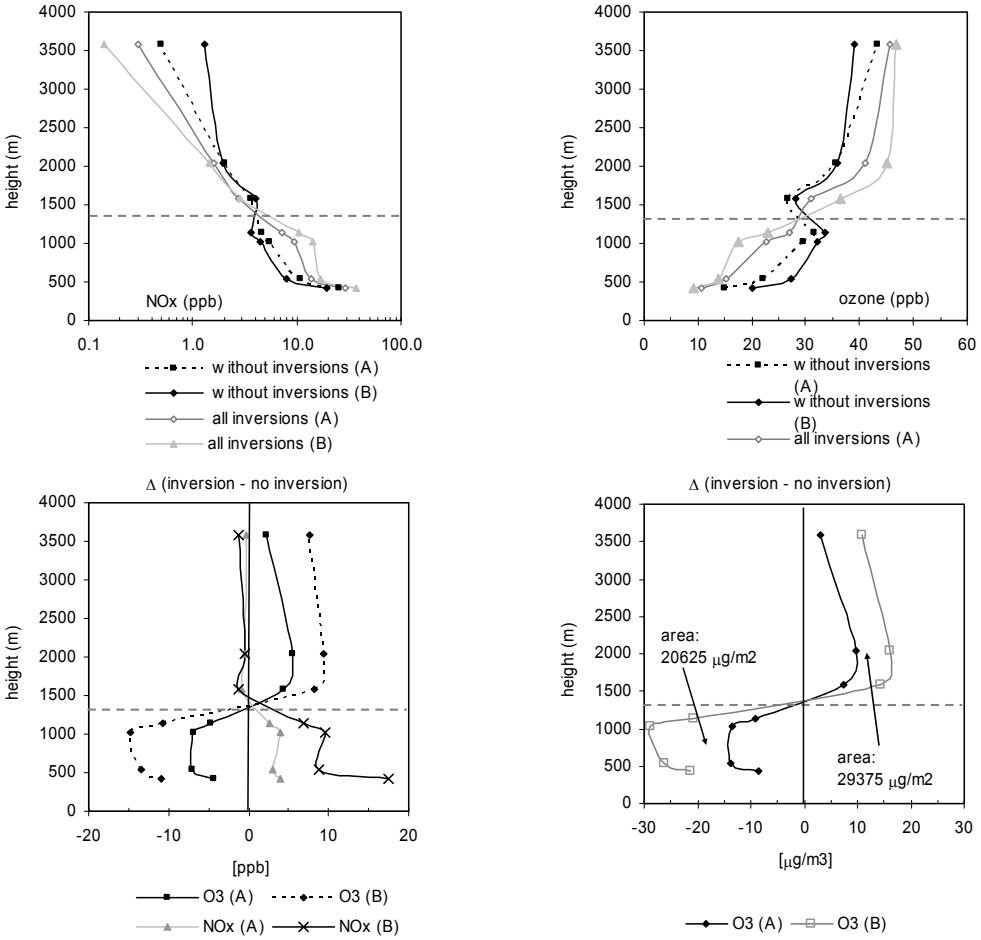


Figure 39: Top: profiles (B) characterized by extremely strong inversions in November and December ("temperature difference between Arosa and Chur" > 0° and "ozone difference" between same station >30 ppb, 10 events) and days without inversions with "temperature difference between Arosa and Chur" <-8° and "ozone difference" between same stations < 10 ppb, 6 events). Profiles are compared with profiles (A) depicted in Figure 21. Bottom: difference calculated between averaged profiles of inversion and no inversion days (ppb and μg/m3). Area below the curve relative to the x-axis is given for ozone profiles (B) calculated with sharper criteria.

	Inversion events (N = 10)		No inversion events (N = 6)	
	O_3	NO_x	O_3	NO_x
Dübendorf	9.2 ± 8.9	37.0 ± 32.7	20.2 ± 9.8	19.5 ± 18.2
Taenikon	13.8 ± 7.9	16.8 ± 8.6	27.2 ± 8.0	8.0 ± 4.4
Rigi	17.5 ± 9.6	14.0 ± 6.8	32.3 ± 5.9	4.4 ± 2.3
Chaumont	22.8 ± 8.3	10.4 ± 4.9	33.5 ± 5.4	3.6 ± 2.6
Davos	36.6 ± 2.9	2.81 ± 2.08	28.2 ± 8.2	4.02 ± 4.14
Arosa	45.1 ± 2.3	1.44 ± 1.83	35.8 ± 5.1	1.93 ± 1.71
Jungfraujoch	46.7 ± 4.7	0.14 ± 0.20	39.0 ± 5.5	1.30 ± 1.36

Table 16: Vertical profiles of ozone and NO_x (B) classified according to the criteria described in text for November and December 2001.

The averaged ozone profiles in Figure 39 could be in a more structured way interpreted as follows. The ozone profiles are representatives for the ozone content in the lower atmosphere situated between the surface and the permanent undisturbed free troposphere (up to about 4000 m). This layer can be regarded as a "box" that can be further subdivided into two layers located above and below an altitude corresponding to temperature inversions (in this case about 1200 – 1500 m). During inversion events air masses located below are not permanently and efficiently replaced by advection of "new" air masses and ozone loss processes (titration with NO and deposition) clearly become visible. When the inversion regime breaks down a general ozone decrease takes place above the former inversion. An ozone increase occurs instead at altitude below the former inversion. This can be understood as vertical exchange of air masses between the lowest and the highest part of the box. In other words the deficit of ozone formed below the inversion can be transported/distributed in the upper part of the box when the inversion breaks down.

The higher amount of ozone calculated in the upper part of the box suggests that the profile "inversion" generally contains more ozone than the profile "without inversion". To explain this result two reasons can be adduced. According to the trajectories ending in Arosa depicted in Figure 38 air masses advected to the location above the inversion layer during inversion events do not seem to present recent contact with fresh emission at lower altitude. At the same moment these trajectories indicate that air parcels can sometimes descend to the station from high altitude (see also discussion in 5.2.1 about origin of high ozone concentration in winter). This can be connected with transport of ozone-rich air. A second reason includes thoughts on deposition effects that occur more intensely during strong advective weather (i.e. during strong mixing). Deposition eventually leads to low ozone content in the profile "without inversion".

NO_x profiles at high altitude only slightly differ in the categories inversion and without inversion. Additionally the difference between both NO_x profiles does not yield such a symmetrical picture as for O3 (Figure 39). This is firstly in contrast to observations made during a passage of a strong front. Indeed very high NO_x concentration can be measured during uplifting ahead a front at high altitude (see section for example 5.1.3.2). These events last only few hours. In such fronts cases the horizontal extension of the above mentioned box concerns only a relatively small region (in the particular case including a region between the Swiss plateau and the alpine region). On the rest of the time vertical transport captures a vaster region (horizontal extension of the "box") than in case of a strong front passage. The ozone and NO_x profiles for days "without inversion" in Figure 39 are most probably in this case also determined by an enhanced ozone and NO_x deposition. Munger et al. (1996) found for example at a rural place that heterogeneous formation of HNO_3, initiated by NO_2 reacting with O_3, is an effective pathway for NO_x removal in winter time and that the supply of HNO_3 and other depositable species does not decrease in proportion with OH concentrations decrease in winter. If NO_x removal is the only or the more important reason for the small difference in NO_x between days "with" and without inversion" at station located at high altitude is an open question.

The analysis yielding the profiles depicted in Figure 39 and based on section 5.2.1 provides generally interesting results about the effect of inversion layer. They however could be further investigated. Indeed ground ozone measurements are more subjected to ozone loss processes than ozone sounding (Naja et al., 2002). In

particular a comparison with Payerne ozone sounding could reveal if similar profiles as in Figure 39 are confirmed over an open space. Also of interest is to see if Figure 35 can be reproduced with ozone sounding. The comparison between both ozone profiles could reveal the possibly strong effect of the orography in uplifting ozone-poor air from the boundary layer into the lower free troposphere.

5.3 Influence of south foehn

5.3.1 Introduction

Foehn is a rather well studied meteorological process typical for the Alpine area. Recent analysis performed at the high alpine station Jungfraujoch showed that this strong advection can sometimes induce a sharp increase in CO and NO_x (Forrer *et al.*, 2000). In the framework of the Mesoscale Alpine Programme (MAP) field phase a rather strong influence of South foehn on ozone concentration is reported for measurement stations located in the plain of the Rhine valley. The arriving of the South flow was connected with increase in ozone concentration (Baumann *et al.*, 2001).

The descending foehn flow at the lee side at lower altitude, which often erodes and replaces a pool of (cold) air, is pronounced for stations in the valley floor closely located to the mountain ridge (Seibert, 1990). Figure 40 shows the typical meteorological situation and the trace gas concentrations in the Reuss valley during a South foehn event. The strong advection from South clearly influences the local meteorology, does not allow primary pollutants to be accumulated near the valley floor and leads to a sharp increase in ozone concentration. Such a trace gas pattern is caused by air parcels coming down from higher altitude after having crossed the Alps (Seibert, 1990). It is therefore interesting to see how measurements at a station like Arosa not being located on the valley floor react to such events with strong advection from the South.

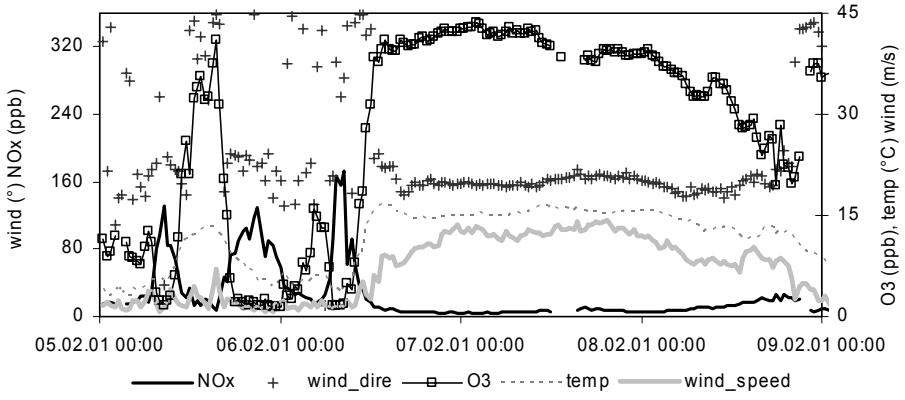


Figure 40: Pronounced foehn event in Altdorf (Reuss valley) during winter 2001.

5.3.2 Foehn Events July 2002

5.3.2.1 Meteorological situation

At the beginning of July 2002 a strong South foehn event occurred as depicted in Figure 41. In total the foehn lasted about 6 days. It was however regularly interrupted by periods with northerly advection. From the 23th of June weather charts (Meteo Swiss) and wind profiles in Payerne show a pronounced westerly advection at 500 hPa, mainly driven by a low pressure system located over Scandinavia. Two cold front systems crossed through the Swiss Plateau and through the Alps on the 24th

and on the night between the 27th and the 28th inducing rain fall and general temperature decrease at several ANETZ stations (not shown).

On the 1st of July Payerne sounding show the presence of a strong SW wind along the whole profile. A constant South wind was observed at Weissfluhjoch. At Gütsch wind speed values up to 12 – 14 m/s were measured. The relative humidity in Chur and in Arosa dropped under 50% and the temperature strongly increased at both stations. These changes took place very rapidly (within few hours). Such changes are typical for the onset of the foehn (Brinkmann 1971; Piringer *et al.*, 2001). Foehn started to blow in the morning hours of the 1st July.

At the end of the 3rd of July foehn broke down a first time due to a cold front crossing the Swiss plateau region from West to East. A short period with northerly wind associated with low temperature determined the meteorological situation until the beginning of the 5th. Then a sharp and general change to South wind occurred for the second time (Figure 41). This period was much shorter and was ended again by a frontal system. On the 6th very low winds up to 7 km (about 6 m/s) were measured at Payerne. On the 7th and on the 8th a high pressure system located over central Europe induced fair weather conditions north of the Alps.

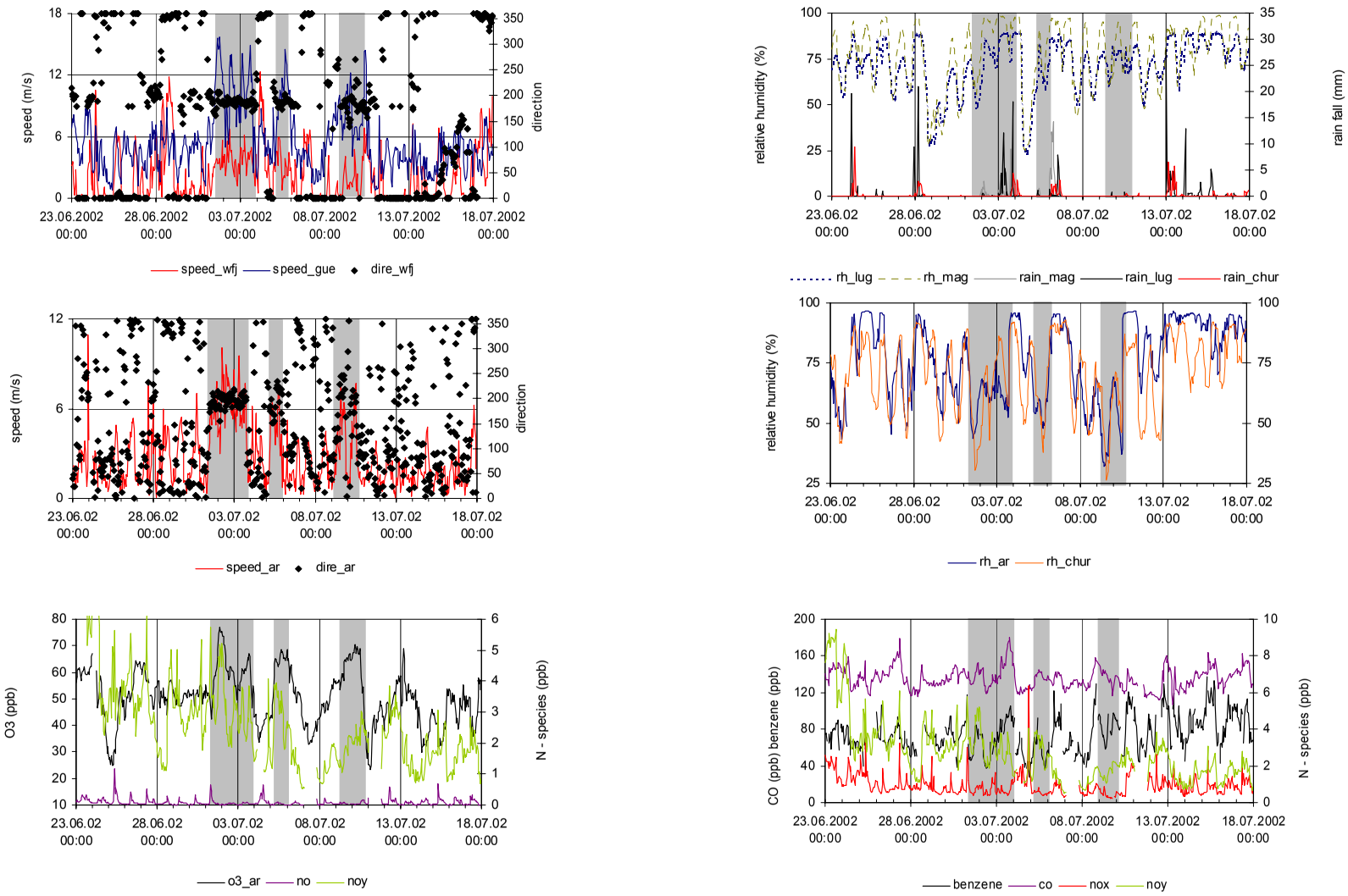
At the beginning of the 9th the South foehn started to blow for the third time. This third event was the less pronounced and more irregular in Arosa as can be seen from the wind measurement (Figure 41). At the end of the 10th a cold front approaching from West to East was again responsible for the definitive break down of the foehn.

The synoptic weather types according to Schüepp (1979) for these days are found in Table 17. South foehn obviously does not occur only within the advective weather type S. In this particular case indifferent weather conditions were prevailing most of the time during the foehn events. This also shows that this weather classification, mainly based on the wind situation at 500 hPa, does not entirely describe the transport processes in the lower troposphere.

Datum	Weather Type	Datum	Weather Type
27.9.2002	I	05.07.2002	I
28.9.2002	W	06.07.2002	N
29.06.2002	I	07.07.2002	I
30.06.2002	I	08.07.2002	H
01.07.2002	I	09.07.2002	I
02.07.2002	I	10.07.2002	S
03.07.2002	S	11.07.2002	I
04.07.2002	N	12.07.2002	I

Table 17: Assignment of measurement dates into different synoptic weather types as described by Schüepp (1979). S = South-advection, W = west-advection, N =north-advection, I = Indifferent, H = Anticyclonic.

Figure 41: Time series for meteorological and chemical parameters at different ANETZ stations and in Arosa during a foehn event (registered in July 2002).



5.3.2.2 ECMWF - trajectories

ECMFW backward trajectories ending in Arosa between the 1st and the 3rd of July show the travel track of air parcels over the European continent (Figure 42). All of these trajectories are originating from South of the Alps. Air parcel arriving in Arosa on the 1st of July stayed about 50 to 60 h in the Po basin (altitude <900 hPa). Air parcels reaching Arosa on the 2nd were characterized by a reduced residence time (<12 h) over the Po basin. After having passed the region of the Gulf of Genoa trajectories descended in the Po basin and eventually ascended to Arosa. Similar observations were made in the morning time of the following day. Air arriving in Arosa was transported fast (in about 24 h) through the Po basin at a rather lower altitude. These trajectories stayed most of the time at lower altitude when they were over Europe.

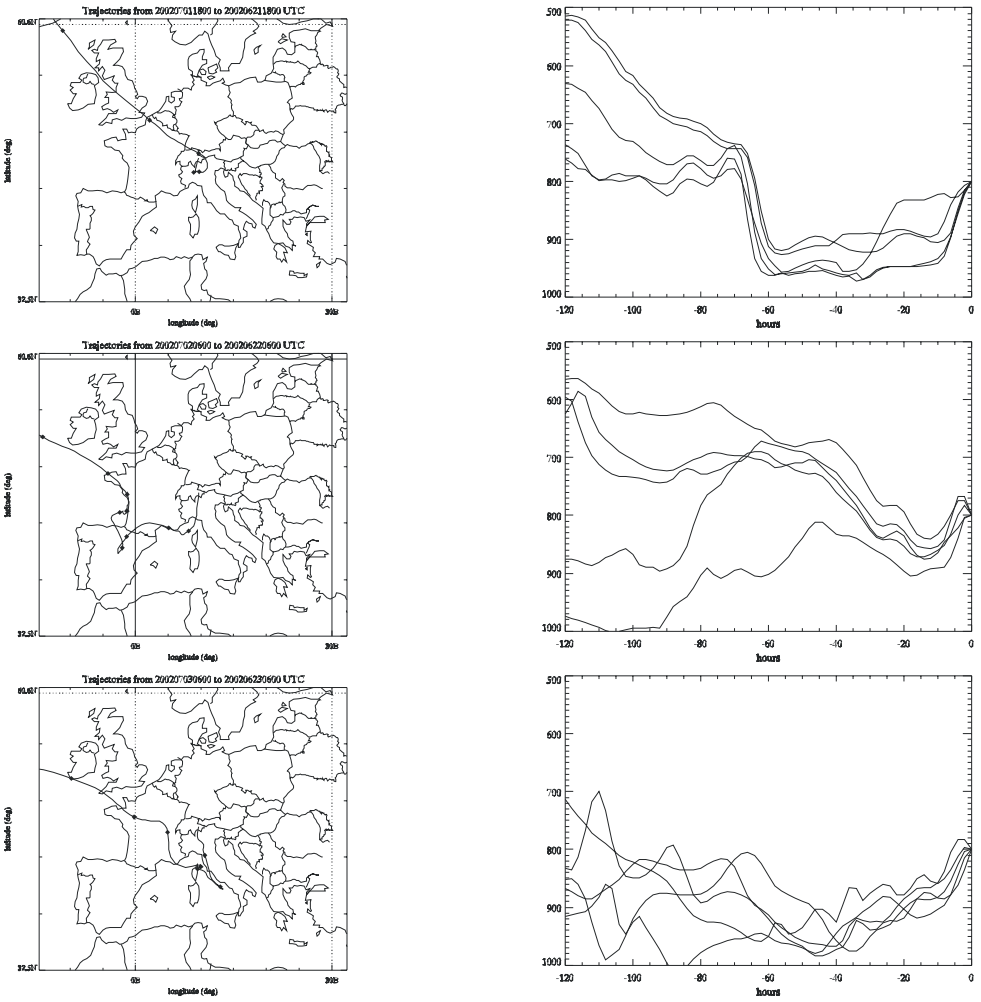


Figure 42: ECMWF backward trajectories ending in Arosa during the 1st foehn event. Marks define 24 hours intervals. For easier understanding a mean trajectory is depicted on the left side, whereas all of the 5 trajectories are depicted on the right side.

5.3.2.3 Chemical measurement in Arosa

The ozone concentration measured in Arosa during the foehn events clearly shows the influence of this strong advection (Figure 41). A sharp increase in ozone concentration of about + 20 ppb occurred during the first and the second foehn event

in Arosa. This result is consistent with the fact that the Po basin is a strong pollutants source region and that the photochemical activity in the Po basin can regularly produce ozone concentrations >100 ppb by clear sky in summer (Thielmann, 2000). The increase induced by the onset of the third foehn event was instead less pronounced. This is most probably due to the effect of the general fair weather conditions prevailing north of the Alps over the 2 previous days. The maximum peak in ozone concentration reached during these three events is of very similar quantity (first event: 76 ppb, second event 68 ppb and third event 70 ppb in Figure 41) and much higher than the median July 2002 value (50 ppb).

In the middle of the first foehn event (2nd of July) there was a quite pronounced decrease in ozone concentration from 75 ppb to about 50 ppb. This occurred on the same day when the sky was covered by clouds over the Po basin (from satellite images). Assuming that loss of ozone along the trajectories was not important this change in ozone concentration could be explained by the fact that air detected at the measurement station travelled fast towards Arosa and was actually only residing few hours before over the covered Po – valley region. Indeed trajectories were travelling very fast (see section 5.3.2.2). This observation suggests that the decrease in ozone of about 15 ppb within the first foehn event could have mainly been caused by a temporarily reduced photochemical activity over the Po basin. This also emphasizes once more the role of radiation for the photochemical ozone production. These conclusions are further supported by the fact that, on the third day of the foehn event, ozone increased as the sky over the Po basin was clear again.

The much reduced trajectory residence times over the Po basin on the 2nd could also be used to explain the observed decrease. After the transport of well aged air (residence time over the Po basin 50 – 60 hours), a mixture containing less polluted air masses rapidly advected from the Tyrrhenian sea could have reached the station. Both explanations (reduced solar radiation and reduced residence time) are possible and do not contradict themselves.

A clear pattern in the variation of primary pollutants in Arosa during this foehn event is not observed (Figure 41). Concentrations of primary pollutants most likely reflect a variable extent of mixing over the Po basin and the strong variable degree of dilution occurring during the rapid advection. The NO-peak due to local emissions in Arosa (see section 6.1) was not detectable during the three foehn events. Considering only the period covered by the three foehn events the NO_y concentration in Arosa was slightly lower when it was raining south of the Alps. CO, NO_x and benzene increased at the beginning of the first foehn event and decreased at the same time as ozone did. This decrease observed could be put in relation to an enhanced contribution of air masses rapidly advected from higher altitudes (see above in this section). At the end of the foehn event carbon monoxide and benzene strong increased again. An increase in benzene and to less extent in CO is observed in the second foehn period. In the third foehn period there was a decrease in CO and no particular variation in benzene (Figure 41).

The ratio NO_x/NO_y instead was similar during all the three foehn periods, values were 0.22 (±0.09), 0.18 (±0.05) and 0.25 (±0.13) respectively. Similarly the ratio NO_y/CO with values 0.023 (±0.006), 0.022 (±0.05) and 0.013 (±0.005) respectively. This clearly indicates that photochemically well aged air masses reached Arosa (see also section 6.4 for explanation on these ratios). The study of Zellweger *et al.* (2002) at the Jungfraujoch reports for summer south foehn events an averaged NO_x/NO_y of ~0.25 which well agrees with the ratio calculated for Arosa. The averaged NO_y/CO at

Jungfraujoch is instead much lower (~0.005) and could be explained by the generally lower NO_y concentration at this site (section 6.3).

The foehn detected in Arosa did not obviously reach the valley floor all the time. This is clearly shown by the variation in ozone and relative humidity at the measurement station in Chur (valley floor). A sharp increase in ozone concentration was observed as soon as the relative humidity dropped below about 45 - 55%. This is a sign that foehn flow reached the valley floor on these moments. At the same time ozone concentrations in Chur and in Arosa were comparable suggesting that air masses in Chur possibly originated from altitudes as similar as those for Arosa.

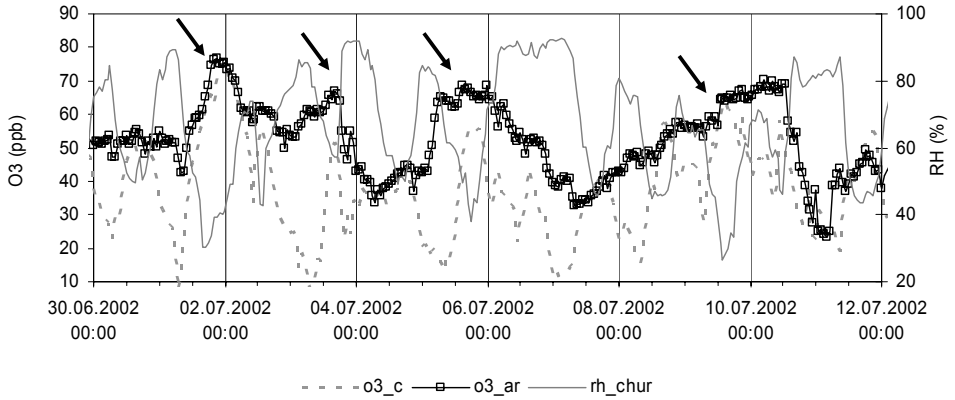


Figure 43: Time series of ozone and relative humidity (RH) in Chur and in Arosa during the foehn period earlier in this section. Arrows indicate a drop in relative humidity; i.e. the arrival of the foehn air in the valley floor.

5.3.3 Periods with South foehn in Arosa

To investigate further the influence of South foehn on trace gas measurements in Arosa it is necessary to find some valuable criteria to delimit such periods. “Sucht man quantitative Kriterien, so gibt es vermutlich gleich viele Versionen wie Föhnbearbeiter” (Burri *et al.*, 1993). With this funny statement the complexity of the problem becomes evident. The Arbeitsgemeinschaft Föhnforschung Bodensee – Rheintal has developed an own foehn definition for the Rhine Valley (Burri *et al.*, 1993). On a mesoscale level two different conditions have to been fulfilled: 1. the South to North advection over the Alps has to be accompanied by a strong positive pressure gradient between South and North and 2. high wind speed of more than 10 m/s have to be measured on measurement stations located on well exposed mountain sites (like Gütsch).

For stations located at the ground of the Rhine Valley empirical criteria were suggested in order to identify begin and end of a foehn event (Burri *et al.*, 1993). Due to the high location of Arosa (at 2035 m), it is however not possible to simply apply the criteria proposed by Burri *et al.* (1993). At a high mountain station like Arosa the typical sharp temperature increase and the strong relative humidity decrease associated with the foehn are usually not so pronounced as in a valley floor location (Dürr, 2002; Gutermann, 2002). The foehn periods in Arosa were defined by criteria that also take into consideration measurements performed in other stations than Arosa (Table 18). The criteria need to be fulfilled simultaneously. This approach aims to delimit periods characterised mainly by strong South advection over the Alps and particularly in the area over Arosa. The pressure gradient was calculated from the ANETZ stations in Zurich and in Lugano (using pressure measurements previously

reduced to sea level according to formula contained in Furger *et al.*, 1989). The pressure gradient value criterion between South and North of the Alps (2.1 hPa per 100 km) was derived from a climatological sudy (Hoinka, 1998).

	Pressure gradient	Wind direction	Wind speed 1	Wind speed 2	Relative humidity
Station	Lugano - Zurich	Weissfluhjoch	Gütsch	Arosa	Chur
threshold	Δ > 2.1 hPa/100 m	[150° – 250°]	> 10 m/s	> 4 m/s	< 65 %

Table 18: Criteria used to select period with South foehn.

These criteria did not include occurrence of precipitation south of the Alps. Indeed precipitation on the windward side was not found not to be a necessary condition for foehn during the ALPEX experiment in the Eastern Alps (Seibert, 1990). As additional criteria the relative humidity in Chur was included. The time series described in Figure 43 show that obviously foehn can reach Arosa without strongly influencing Chur. For this reason a rather high value of 65% was set if compared with the values (45 – 55 %) observed when the foehn clearly reached the valley floor (Figure 43).

According to the above described criteria, 882 hours of South foehn were found in Arosa. This corresponds to about 5% of the 2 years considered in this work. Hours with foehn in Arosa were distributed in the 4 seasons as follows: spring 300 h, winter 210 h, fall 279 h, whereas a minimum was found in summer (103 h).

Most of the foehn events occurred as expected during days with south advection as defined by the weather type classification by Schüepp (1979). A not negligible amount of foehn events were however found also during days with prevailing west advection and during indifferent conditions (Table 19).

Weather type	Hours with foehn	Weather type	Hours with foehn
East	-	Cyclonic	20
South	449	Indifferent	199
West	98	Anticyclonic	25
North	3	Mixed	30

Table 19: Weather type according to Schüepp (1979) during the foehn events detected in Arosa.

Backward trajectories arriving in Arosa were calculated (early morning at 06 UTC for the 2 years). A set of preliminary results showed that one trajectory a day was not sufficient to describe the flow pattern during South foehn. This is plausible considering that South foehn can rapidly start to blow and completely modify the flow pattern which was present just before the foehn beginning (Brinkmann, 1971). Trajectories were therefore selected only for events occurring ± 6 h relative to the arrival of the trajectories at the measurement site. This analysis only included 66% of the selected foehn events; it gave however good information about the origin of the air masses arriving in Arosa during South foehn (Figure 44 which reports only the last 48 h before the arrival in Arosa). It turned out that almost the total amount of the trajectories was clearly coming from the South sector. Most trajectories arrived in Arosa after having travelled over the Po basin usually coming from a region S - SW of the Po basin (ligurian Apennine). Practically none of the trajectories were coming from the Adriatic region. About 48 h before arriving in Arosa many trajectories were still over the Tyrrhenian and the Mediterranean seas. Thus the air masses arriving in

Arosa were often rapidly advected over the Po basin (Figure 44). The altitude of the trajectories shows that air masses during foehn events did not necessary originate at very low altitude in the boundary layer South of the Alps (<900 hPa). Indeed the rising motion from low altitude is not a necessary condition for development of South foehn according to Seibert *et al.* (1990). This study reports that air typically originates from a level of 2000 m in the South. None of the selected trajectories give indication about upper troposphere or stratospheric origin of air masses.

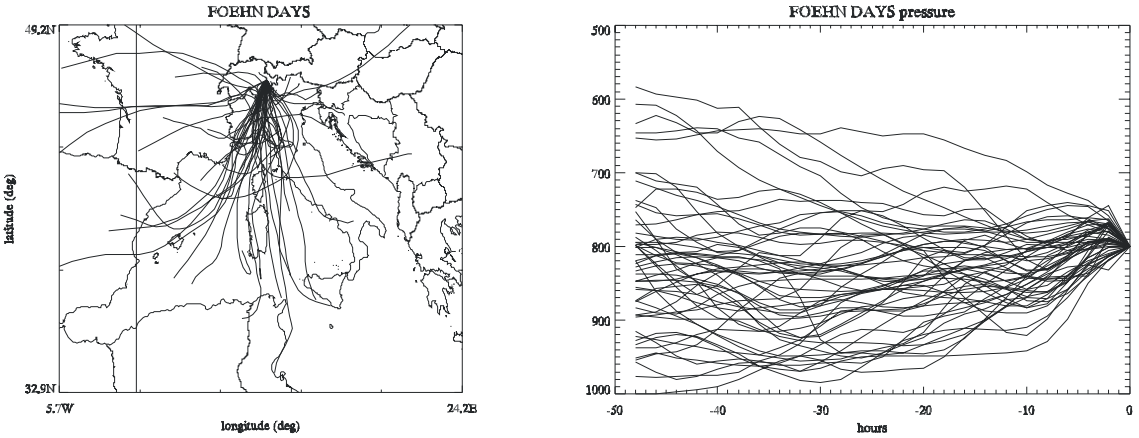


Figure 44: Trajectories during foehn events occurring ± 6 h relative to the arrival of the trajectories in Arosa (for easier understand only case from March 2001 to June 2002 are depicted).

Compared with the monthly median the ozone concentrations during the selected foehn events show a generally high variability (Figure 45). So in each season foehn can induce higher as well as lower ozone concentration than the monthly median. However in summer, spring and fall most of the selected foehn events cause a positive difference in ozone concentration. This is most pronounced during summer (about 10 ppb for median value). This shows that foehn events in summer are usually associated with an increase in ozone as it was also found in the event described in section 5.3.2.3. Elevated ozone concentrations are supposed to have formed photochemically mainly in the Po basin and also during the transport toward the Alps (Seibert *et al.*, 2000). In winter the same difference is much smaller (Figure 45).

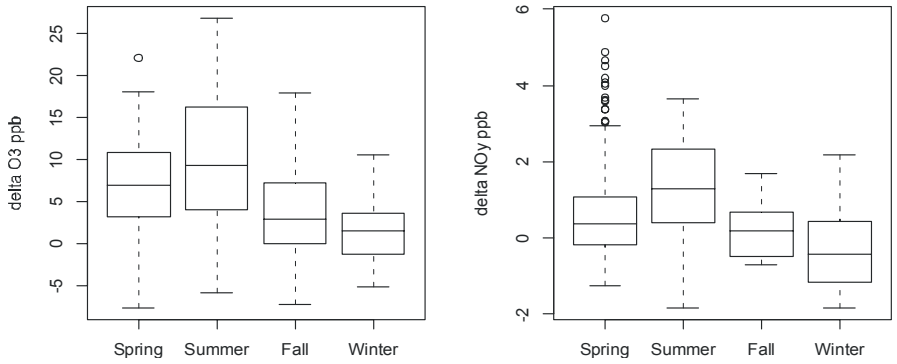


Figure 45: Boxplot of the difference between ozone and NOy concentration in Arosa during foehn and their monthly median (for foehn events without rain south of the Alps).

This result can be explained by a reduced photochemical activity that occurs during the cold season. No clear evidence of titration due to advection of highly polluted and

ozone-poor air masses was found. NO_y shows similar tendency as ozone. Foehn events in summer are connected with enhanced NO_y concentration in Arosa. In spring this tendency is much less evident and no difference is observed, compared to the median value, in the cold season. Points with a large difference are associated with foehn episodes found in late spring (end of April and May). For the foehn events (where both NO_y and ozone measurements were simultaneously available) the difference ΔNO_y between NO_y during foehn and the NO_y monthly median against the difference ΔO_3 between ozone during foehn and the ozone monthly median was plotted. The season in which a foehn event occurred and the occurrence of precipitation in the South edge of the Alps, influences the distribution of points in Figure 46. Foehn event in summer are most of the times related to both high ozone and high NO_y concentrations (Figure 46).

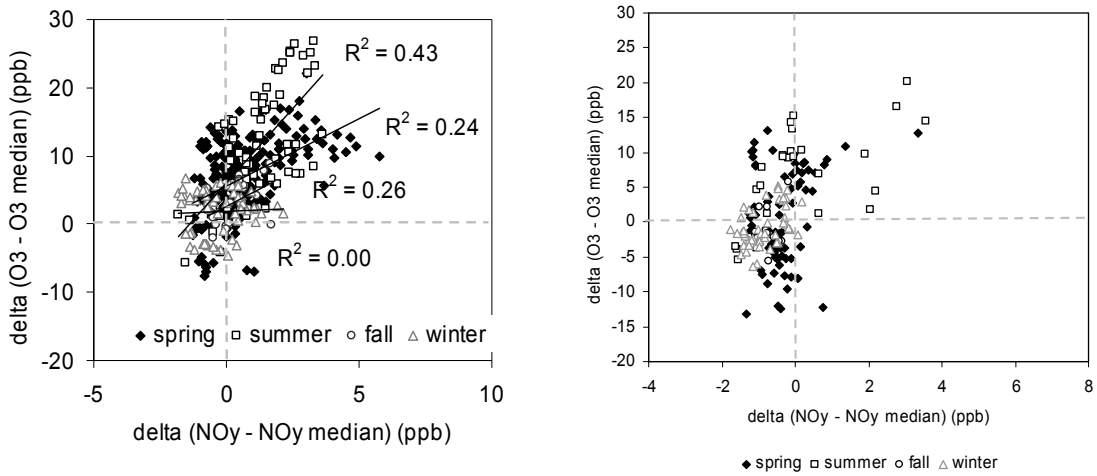


Figure 46: Ozone and total reactive nitrogen in Arosa during South foehn compared to monthly median. Left: cases without precipitation in Magadino and in Lugano (r = 0 mm). Right: cases with precipitation in Magadino or in Lugano (r>0 mm). The small availability of NO_y measurement in fall explains the small number of hours with foehn within this season. To discriminate events with/without precipitation data from the ANETZ stations in Lugano and in Magadino were considered. A time shift of three hours before the ozone and NO_y measurement in Arosa was taken into account.

In case of precipitation the number of cases with a positive NO_y difference strongly decreases. This is most pronounced in spring and summer and can be explained by the fact that the highly soluble NO_y species (as HNO_3) might be efficiently removed by wet deposition (Colett *et al.*, 1993; Munger *et al*. 1996). For the foehn cases without precipitation, scatter plots between ozone and NO_y show a positive correlation which is highest in summer suggesting the photochemical origin of the ozone transported to Arosa from the Po basin. In spring the correlation is slightly lower and in winter time no positive correlation was found. This result agrees with measurements performed at Sonnblick (3106 m) by Seibert *et al.* (1998) which show that for cases of advection from the Po basin high concentration of sulphur dioxide are often limited to dry events. At Jungfraujoch Forrer *et al.* (2000) found more pronounced trends for foehn cases showing strong and negative correlations between ΔCO and ΔO_3 during winter months and a positive correlation between ΔCO and ΔO_3 in the warm season (Δ being defined as in this study as difference between actual measurement and median value). In winter time a strongly negative ΔO_3 (up to 20-30 ppb) together with ozone concentration <30 ppb could be observed several

times in the period 1996 - 1997 at Jungfraujoch (Forrer *et al.* 2000). This was clearly not the case in the two years 2000-2002 for Arosa measurements (Figure 46). This possibly suggests that Jungfraujoch is more sensitive to (pollutants) transport from the Po basin than Arosa is. During summer instead higher values of ΔO_3 were reached in Arosa (Figure 46) than at Jungfraujoch (up to about 10 ppb at this latter station, Forrer *et al.* 2000).

The correlations given by Forrer *et al.* (2000) are stronger than those found in Arosa. The positive summer trend in Arosa provides however evidence that O_3 rich air transported by the foehn flow can descend in the Arosa basin without simply flowing over it. Such a motion can however not be resolved by ECMWF trajectories (Figure 44) as the real topography at the receptor site is only coarsely described by this model.

5.3.4 Ozone in Chur during foehn events

It was previously observed (section 5.3.2.3) that, during foehn, ozone concentrations in Chur did not significantly differ from those measured in Arosa. Obviously in case of strong foehn events the vertical ozone profile shows almost no gradient. However this only happened when the rather irregular foehn flow reached the valley floor. To detect the occurrence of foehn events in Chur relative humidity is the most suitable parameter. In addition to the criteria discussed in the previous section the parameter relative humidity was newly set (45%). The amounts of hours selected were reduced from 882 h to 486 h, thus about only 55% of the selected foehn events in Arosa reached simultaneously the valley floor in Chur. Potential temperature can be used as a tracer to detect air masses having similar thermodynamic properties and can give further information about the origin of air masses (Weber & Prevot, 2002). This holds only in case of adiabatic processes like during foehn when potential temperature is conserved along the air path (Seibert, 1990). Differences in potential temperature between Arosa and Chur are generally smaller during foehn events and more centered on zero relative to the total amount of data (Figure 47). The same holds also for ozone that can be as well used as a tracer.

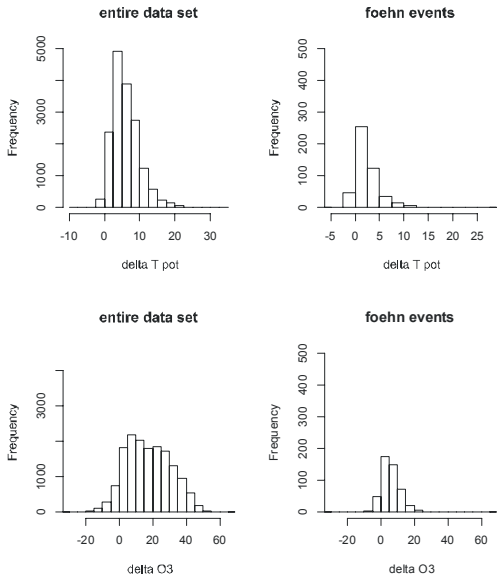


Figure 47: Frequency distribution in hours of differences in potential temperature (interval 2.5 K) and in ozone concentrations (interval 5 ppb) between Arosa and Chur for the entire data set

(left) and during foehn events in Arosa and in Chur (right). Positive values indicate potential temperature and ozone concentrations being higher in Arosa.

The differences in ozone between the two stations can be normally very important but are reduced during foehn events (Figure 47). Nevertheless the positive delta O_3 shows that concentrations at 2000 m are often higher. This can be explained with ozone dry deposition occurring during the transport down to the valley floor. The difference in ozone concentrations between foehn periods and monthly median values in Chur is usually strongly positive (Figure 48). The median value calculated for this difference is similar in each season (>10 ppb). Compared to Arosa the increase induced by foehn in Chur in winter and fall is clearly much higher. During these seasons strong inversion layers develop over the Swiss Plateau and over the Rhine Valley region resulting in low median ozone concentration in Chur. Ozone concentrations increase as soon as the foehn flow removes the pool of cold and ozone-poor air.

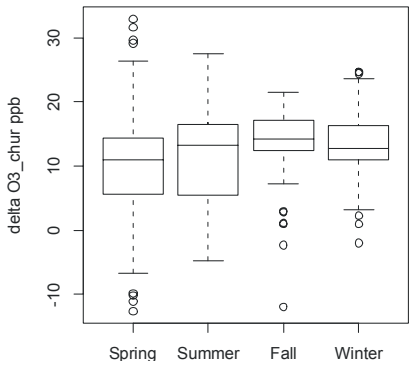


Figure 48: Boxplot of the difference between ozone concentration during foehn and its monthly median in Chur.

Figure 49 shows that the diurnal variation in ozone concentration normally observed at lower altitude (Chur) is almost absent during foehn and that the increase is the highest for night time and early morning, while ozone is usually low without foehn.

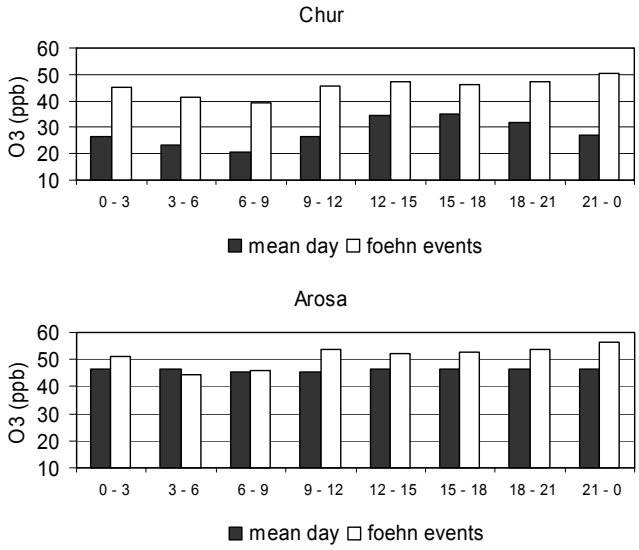


Figure 49: Mean diurnal variation in ozone concentration during foehn as compared to the annual daily variation in Chur and in Arosa (averaged all over the year).

To a large extent, this observation can be understood given the fact that high wind velocities and turbulence reduce the effectiveness of the processes which lead to a minimum in the nocturnal O_3 concentration in a valley floor (dry deposition and titration by NO). In Arosa no average diurnal variation in ozone is found on an annual basis and the increase due to foehn events is less pronounced.

5.3.5 Ozone in Arosa and at Mt. Cimone during south foehn

The results found in the previous section identify the Po basin as a source for high ozone concentration in the Alpine region in the warm season. This result emphasizes previous results from studies showing the Po basin as a region characterized by large pollutants emissions in which extremely high ozone concentration are regularly reached in case of fair weather (Prevot *et al.*, 1997; Thielmann, 2000). In a foehn case in late spring described elsewhere the authors found that in the foehn area north of the Alps ozone concentration was higher than at Monte Cimone, located in the upstream flow south of the Po basin (Seibert *et al.*, 2000) (Figure 51). A difference of 10 – 20 ppb was attributed to ozone production in the Po basin and / or in the South – alpine valleys. The Mt. Cimone is located at 2165 m in the ligurian Apennine, thus at an altitude comparable with Arosa. Ozone measurements at this station can be used to estimate tropospheric ozone background in South Europe (Bonasoni *et al.*, 1993). Figure 50 shows that ozone concentrations are higher at Mt. Cimone than in Arosa during the warm season. This is not only the case for the monthly average values, but also for maximal values. The location of Mt. Cimone in the south and its close proximity to the Po basin are the most probable causes for these enhanced concentrations. In the cold season (from October to March) ozone concentrations at both sites become much more similar. In winter, an inversion layer frequently formed over the Po basin (Baumann et al., 2001; Seibert, 1990; Seibert *et al.*, 1998) and similarly to what seen for Arosa the Mt. Cimone can be considered as often decoupled from the boundary layer.

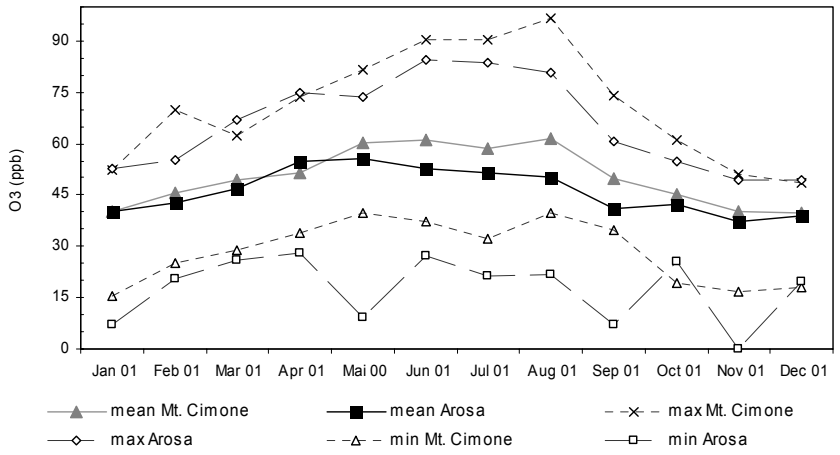


Figure 50: Seasonal variations in ozone concentrations in Arosa (2035 m) and at Monte Cimone (2165 m), (hourly averages for the year 2001 were used).

For the different foehn cases selected and described in the previous section ozone concentrations in Arosa (downstream) were compared to those registered at Mt. Cimone (upstream). The analysis was restricted to events for which a backward trajectory was available: the trajectory had to cross a circular area with a radius of 2.7° around Mt. Cimone (this corresponds to a maximal distance of about 215 km

between Mt. Cimone measurement station and the closest point of the trajectory). Therefore the analysis was restricted to events where air parcels traveled from South to North and crossed the Apennine area before moving above the Po basin. The ozone concentrations in Arosa at the time of foehn detection were compared to ozone concentrations at Mt. Cimone measured at the time of the closest passage of the trajectory (at both sites averaged over 3 h). To ensure a sufficient number of cases for climatology the months spanning from April to September were considered as warm season while the months October to March represented the cold season.

Figure 51 shows the foehn case of the 29th of April 2001. In early morning a rather strong foehn was losing its strength. However ozone concentrations in Arosa were still about 10 ppb higher than the monthly average and amounted to about 65 ppb. According to the trajectories ending in Arosa air parcels were coming from the South and were crossing the Apennine region about 18 hours before arriving in Arosa. At that time (early morning on the 28th) at Mt. Cimone a wind direction between 180° and 290° was observed along with an average ozone concentration of about 56 ppb. The ozone increase of about 10 ppb, occurred in the air parcel between Mt. Cimone and Arosa, can be thus attributed to the Po basin contribution. Theoretically the increase could be the result of photochemical activity and/or of mixing with ozone-rich air from the boundary layer over the Po basin. In any cases this suggests that a strong ozone increase took place in the considered air parcel on its last day on the way to Arosa. This result is also strengthened by the fact that satellite images on the 28th showed a cloudless sky over the Po basin and south of the Alps which was certainly favorable for ozone production.

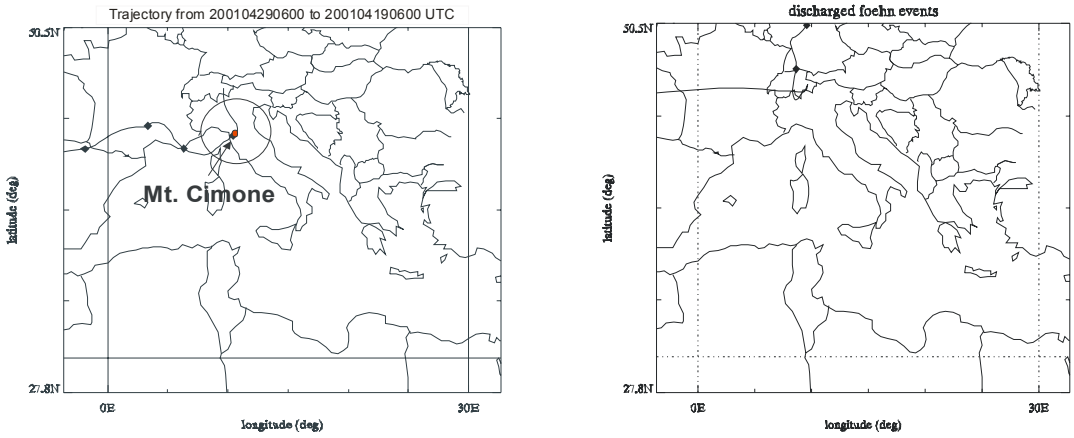


Figure 51: Left: foehn event on the 29th of April 2001 with passage close to Mt. Cimone (2165 m). Right: two foehn cases registered in Arosa excluded from the analysis (see text). Backward trajectories end in Arosa at 06 UTC.

Figure 51 also shows an example of two foehn events that were excluded from this analysis. Although clear evidences of foehn were observed in the alpine region on the 5th of January 2001 the trajectory path indicate that air parcels arriving in Arosa did not cross the Po basin but directly came from the West after a short passage above southern Switzerland. Also during the foehn event of the 27th of February 2001 trajectory clearly indicates that air parcel did not cross the Apennine area. Indeed meteorological measurements at stations in the alpine region showed that foehn had just started to blow early morning on the 27th. Air parcels previously advected from the North had changed suddenly their direction (Figure 51). Table 20 shows the result for all foehn cases considered in the analysis. In the photochemically more active period of the year it turned out that South of the Po basin ozone

concentrations were on average lower than in Arosa during the selected foehn cases. Out of the selected 23 cases only 3 showed ozone values higher at Mt. Cimone than in Arosa. The ozone excess in Arosa was 5.6 ppb (average over all foehn cases, Table 20).

Considering that during the warm season ozone concentrations at Mt. Cimone are usually higher than in Arosa (Figure 50) the result becomes even more evident. During the South foehn cases selected air parcels originated mostly from the Tyrrhenian sea region and had not been in recent contact with a plume of a big agglomeration. After having passed the mountainous Apennine region air parcels were transported over the Po basin towards the Swiss alpine region. The passage took place rather fast, according to trajectory the mean duration amounted to less than 1 day (~17 h ±13). As for the 30th April case this increase in ozone between both stations can be explained both by photochemical production, occurring during the transport, or by mixing with ozone-rich air present over the Po basin.

	O_3 Arosa (ppb)	O_3 Mt. Cimone (ppb)	Difference in O_3 (ppb)	# foehn cases
Apr – Sep	61.4 ± 6.7	55.8 ± 5.1	+ 5.6 ± 4.7	23
Oct – Mar	40.2 ± 5.5	44.2 ± 4.2	- 4.0 ± 5.1	37

Table 20: Averaged ozone concentrations and their standard deviations South and North of the Po basin during foehn cases (data from September 2000 to December 2001). Difference in ozone between both stations can be regarded as variation along the trajectory. Data are subdivided into a warm season (from April to September) and into a cold season (from October to March).

Table 20 indicates how the averaged ozone increase is accompanied by a rather large value in standard deviation (4.7 ppb). It is interesting to note that for those 11 cases in which trajectories were over the Po basin during the night (residence time between Mt. Cimone and Arosa < 12 h, trajectories arriving in Arosa at 06 UTC) the increase was only 3.7 ± 5.4 ppb, whereas for the 12 cases in which air parcels were over the Po basin during day time (residence time > 12 h) the increase amounted to 7.5 ± 2.8 ppb. Not only the increase but also the absolute ozone concentration in Arosa (65.0 ± 5.6 ppb) was higher during foehn events involving an air parcel passage over the Po basin during daytime. When air parcel were over night over the Po basin ozone concentration was lower (54.7 ± 14.3 see also Figure 52). This suggests that ozone content of an air parcel traveling towards Arosa is dependent on its crossing time over the Po basin. At night ozone production in an air parcel is not just stopped. Indeed if mixing of foehn air with ozone-poor air from the nocturnal inversion layer occurs, ozone in the air parcel decreases. In this sense note that the 3 cases in which ozone concentration in Arosa were lower than those at Mt. Cimone denote a residence time between both station < 12 h.

Another more “dynamical consideration”, already mentioned in section 5.3.2.3 could also be used to discuss the less pronounced increase during night passage over the Po basin. Less polluted air from the sea could be more rapidly transported to Arosa in case of residence time <12 h.

During colder months the opposite tendency was observed relative to what found for the warm season (Table 20). Ozone concentrations measured in Arosa during foehn events in the cold season were on average lower compared to those measured at Mt. Cimone (- 4 ppb, with only 5 cases out of 37 showing a higher concentration downstream). This is consistent with a strongly diminished photochemical activity during these months. In a foehn case registered in October it was shown that foehn

flow was crossing the Po basin above a capping inversion whose ozone content was less than 25 ppb. Ozone concentrations measured above this inversion corresponded to values measured in the foehn air north of the Alps and was similar to ozone concentration observed at Jungfraujoch (Baumann *et al.*, 2001). The comparison performed in the present study suggests that also ozone titration processes and/or mixing with ozone-poor air from the boundary layer over the Po basin took place while air parcels were moving towards Arosa.

The amount of ozone destruction was probably dependent on the extent of the mixing between foehn flow with ozone-poor air from the boundary layer of the Po basin and, thus, on the stability of the atmosphere above the Po basin as suggested by the high values of standard deviation (Table 20). The result is in agreement with observations made at Jungfraujoch showing extremely low ozone concentration (<30 ppb) during some foehn events in winter (Forrer *et al.* 2000).

Figure 52 depicts all the foehn cases summarized in Table 20. In this Figure ozone values and differences in ozone concentrations between Arosa and Mt. Cimone are plotted against the maximal pressure of trajectories over the Po basin (i.e. the lowest altitude reached by the air parcel). One might expect a chemical signature in the air parcel if interaction between air parcel and boundary layer takes place.

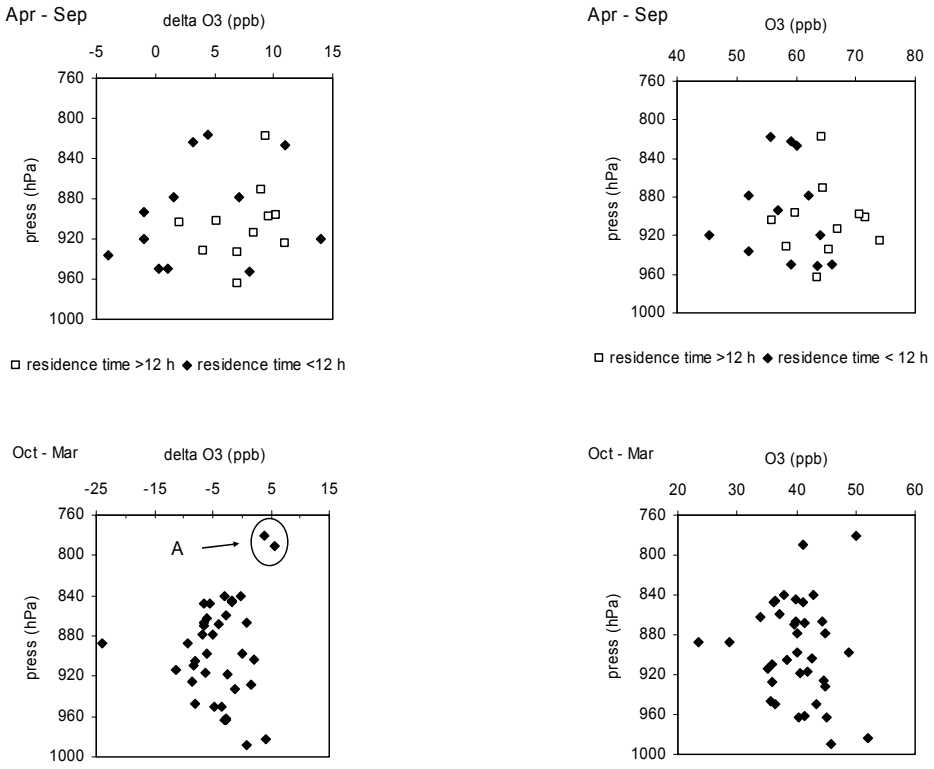


Figure 52: Scatter plots representing O_3 (ppb) and maximal pressure (hPa) of trajectories over the Po basin. Left: ozone difference between Arosa and Mt. Cimone (ppb). Right: Absolute ozone concentration in Arosa. Data are subdivided as in Table 20 in a warm season (from April to September) and in a cold season (from October to March). Case A is discussed in text and includes the foehn events occurred on the 24th of December 2000 and on the 2nd of January 2001. Backward trajectories end in Arosa at 800 hPa.

This should be more pronounced in the cold season or in the warm season when passage over the Po basin occurs during night and at very low altitude. In this case ozone is expected to be reduced by deposition and titration with fresh emission (see section 2.1). According to the trajectories of the two foehn events referred in Figure 52 as A air parcels were traveling respectively 10 or 20 hours over the Po basin at a rather high altitude and the positive difference in ozone concentration between Arosa and Monte Cimone did not indicate any titration events occurring in those air parcels but even suggested a contribution of ozone from high altitude. In one of the two cases the ozone measured in Arosa reached even 50 ppb which is about 10 ppb higher than the monthly median value in Arosa. Therefore in both south foehn cases a contact with the ozone-poor boundary layer can be excluded.

Figure 52 shows that for the entire data set a clear pattern is not recognizable. From the results no dependence can be found between altitude of trajectory over the Po basin and ozone concentration in Arosa. A possible explanation could be that the ECMWF trajectories did not enough reproduce the vertical air transports near the Alps.

The extended analysis of foehn events in Arosa has shown the strong impact of the Po basin on the ozone concentration north of the Alps (Arosa and Chur). According to the definition adopted in this study south foehn occurred about 5% of the time at the investigation site Arosa. In chapter 7 south foehn issues will be addressed by comparing ozone concentrations during foehn with air parcel residence time over Europe. The result will once again show the strong impact of the Po basin on the ozone measured in Arosa.

5.4 Summer episodes

5.4.1 Ozone episode July 2001

5.4.1.1 Meteorological situation

From the 23rd of July to the 1st of August 2001 increasing ozone concentrations were measured in Arosa. Before the period advective weather accompanied by the passage of several fronts prevailed over the European continent. Fair weather dominates over large part of the continent on the 22nd (stable high pressure system). The only perturbance in this fair weather period was caused by the passage of a weak cold front in the second half of the 23rd. This period with extreme weak synoptic flow was influenced from the beginning of August more and more by the development of a stronger west and southwest flow which resulted in an extended south foehn event in Arosa from the 2nd (Table 21).

Time	Wind - direction at 500 hPa	Wind - speed at 500 hPa (m/s)	Wind - speed JFJ (m/s)	Wind - speed WFJ (m/s)	T Arosa	RH Arosa	Radiation Arosa (W/m2)
17.07	W	15 – 20	5	5	5.9	87	515
18.07	SW	25 – 30	7	5	6.3	86	99
19.07	SW	15 – 20	9	5	6.0	95	326
20.07	NW	5 – 10	9	12	3.2	92	74
21.07	NW	10 – 15	9	6	7.0	78	759
22.07	#	5 – 10	7	6	13.2	46	870
23.07	W	5 -10	5	5	13.6	61	848
24.07	#	5 -10	5	6	10.4	80	302
25.07	#	5 -10	3	5	12.4	74	767
26.07	#	5 -10	4	4	13.9	68	740
27.07	#	5 -10	3	4	14.1	67	560
28.07	#	0 – 5	4	5	14.2	64	652
29.07	#	5 -10	3	5	14.6	68	628
30.07	N	5 -10	6	5	14.0	72	657
31.07	#	5 -10	6	4	16.5	65	791
01.08	W	5 -10	2	4	16.7	69	819
02.08	SW	10 – 15	5	7	16.9	62	789

Table 21: Wind direction at 500hPa: # no predominant wind direction. JFJ = Jungfraujoch, WFJ = Weissfluhjoch. Daily mean of temperature (T) and relative humidity (RH) in Arosa.

Trajectories ending at 06 UTC in Arosa show that air parcels between the 23th of July and the 1st of August moved towards the Alps from the North of Europe (Figure 80).

5.4.1.2 Chemical measurement in Arosa, Taenikon and Jungfraujoch

The case represents a typical summer ozone event which can occur by enduring of high pressure conditions. These periods usually go out from bad weather conditions. Chemical measurements in Arosa revealed a strong increase in ozone from < 40 ppb on the 23rd to more than 80 ppb on the 30th early morning. This period was followed by a decrease down to 50 ppb; thereafter during the second half of the 31st ozone concentrations increased again (Figure 53). Taking into account only the period with clear good weather conditions from the 25th the ozone increase amounted to 4.5-5

ppb a day whereas the increase in NO_y and CO were about 0.5 ppb and 4-4.5 ppb a day.

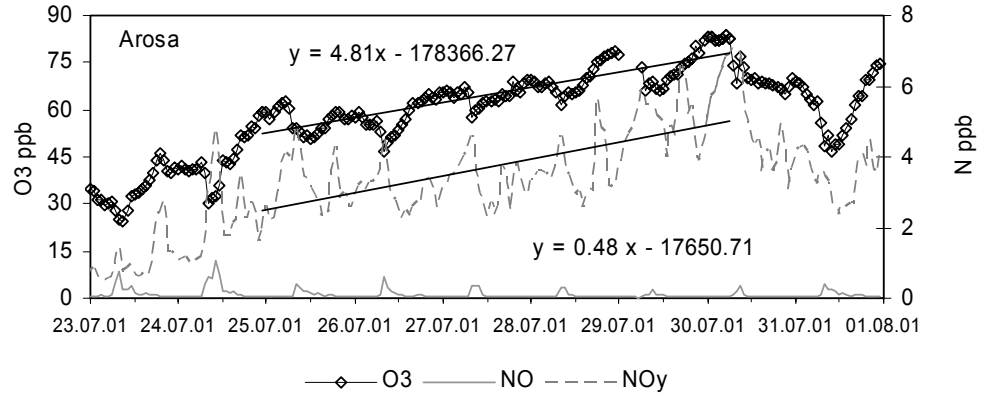


Figure 53: Time series of ozone, NO_y and NO in Arosa at the end of July 2001.

A comparison with the measurement stations Taenikon in the Swiss plateau and the high alpine site Jungfraujoch shows that the ozone increase took place on both locations too (Figure 54).

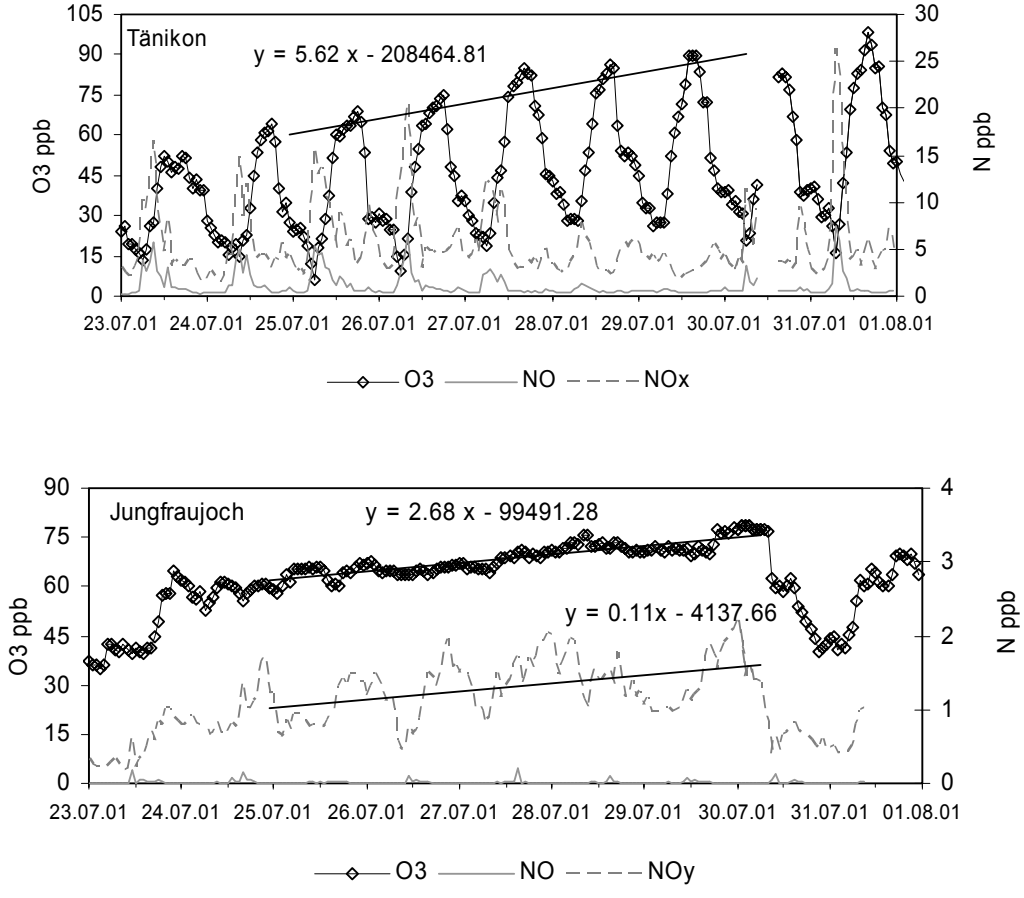
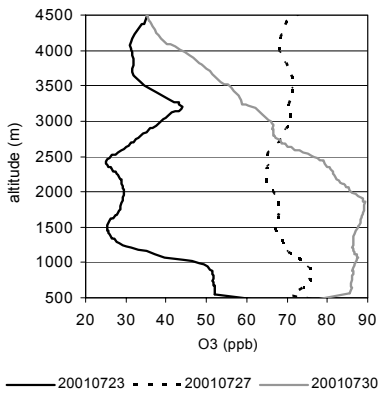


Figure 54: Time series of ozone, NO_y^* and NO at Taenikon ($^*NO_x$) and Jungfraujoch at the end of July 2001.

At the station Taenikon the pronounced daily variation in ozone (40 – 55 ppb) was caused by the development of a stable nocturnal inversion layer (section 2.3.1). Considering only ozone concentrations during day time (11-18 CET) the increase of about 5 – 6 ppb per day was only slightly higher than the increase registered in Arosa in the same period. During the afternoon ozone concentrations in Taenikon were even higher than in Arosa and at Jungfraujoch. The NO_x concentrations did not show any increase during this period: during the weekend on the 28th and 29th even lower concentrations were measured than during previous days. At Jungfraujoch the increase in ozone between the 25th and the 30th was less pronounced but still significant and amounted 2.5-3 ppb a day. The same appeared for NO_y whose increase amounted 0.1 – 0.15 ppb per day.

In the morning time of the 30th a strong drop in ozone, NO_y and CO was observed at Jungfraujoch and in Arosa. This was most pronounced at Jungfraujoch where the ozone concentration decreased within 13 hours from 77 ppb to 41 ppb. This sudden change could not be explained by a passage of a front as during these days fair weather condition prevailed over large part of the continent (Table 21). Similar observations at Jungfraujoch were made by Nyeki *et al.* 2000 who found that during phases with weak synoptic flow advection from NW direction at 500 hPa can replace polluted air masses by clean free troposphere influenced air (see also wind direction at 500 hPa on the 30th in Table 21).

Figure 55 shows the evolution in ozone concentration in the lower atmosphere during these days. At altitude above 2.5 km the ozone sounding of the 30th indicated lower concentration than on the 27th and showed from about 2 km a strong negative gradient (about 20 ppb per 1 km). The evolution was consistent with the time series in Arosa and Jungfraujoch (Figure 55) and indicated that a large phenomenon was responsible for the strong decrease above 2 km. The only pronounced discrepancy in the comparison between ground measurement and sounding was found on the 30th at an altitude of about 2 km (15 ppb). Note however that only few hours before ozone concentration in Arosa was higher than 80 ppb (Figure 54) and that the sounding registered an extremely strong decrease in ozone concentration with increasing altitude.



Payerne Soundings 12 UTC	O_3 (ppb) Arosa	O_3 (ppb) Sounding at 2.0 – 2.1 km
23.07.2001	33	29
27.07.2001	62	65
30.07.2001	69	84
	O_3 (ppb) Jungfraujoch	O_3 (ppb) Sounding at 3.5-3.6 km
23.07.2001	35	41
27.07.2001	71	69
30.07.2001	53	58

Figure 55: Ozone soundings at Payerne (Meteo Suisse) and comparison with ozone concentration in Arosa and Jungfraujoch (mean 11 – 13 CET).

Trajectory calculation performed in Arosa (arrival at 06 UTC) and Jungfraujoch (arrival at 08 UTC) showed at both locations a general increasing in air parcels

residence times over Europe from the 23rd to 29th most pronounced in Arosa (Table 22). Trajectories ending at Jungfraujoch on the 30th and on the 31st suggest instead that air was for a certain while transported very fast over Europe at an altitude of about between 570-650 hPa from the north Atlantic region. Thus transport could explain this decrease at Jungfraujoch. Logan, 1999, analysing ozone sounding measurements of the years 1980 to 1993, suggests an ozone concentration of about 50-60 ppb at this latitude (50-60°N) during July. Wotawa *et al.* (2000) gives for the North Atlantic region a typical ozone concentration of about 46-52 ppb, however for a layer below 2500 m.

Trajectories ending in Arosa do not show any decrease in residence time on the 30th whereas a slight decrease took place on the 31st but it was not as pronounced as at Jungfraujoch. Also the altitude of the trajectories (between 800 – 900 hPa) did not suggest an origin from particular high altitude. This large discrepancy is somehow unexpected as during these two days (30th and 31st) similar ozone concentration were measured at both sites. The most interesting feature on this event is that despite these trajectories the ozone sounding and the measurement at Arosa showed that the influence of advection of clean air from the north was recognisable at altitude much lower than Jungfraujoch, typically until 2000 m. Ozone at Jungfraujoch and Arosa decreased to about 40-50 ppb during this event. This concentration could be an estimate for the summer ozone concentration less disturbed by European emission ("background").

	Arosa		JFJ			Arosa		JFJ	
Time	Res.time (d)	O_3 (ppb)	Res.time (d)	O_3 (ppb)	Time	Res.time (d)	O_3 (ppb)	Res.time (d)	O_3 (ppb)
23.07.2001	2.7	30.5	2.4	41.2	28.07.2001	5.3	67.9	4.7	74.5
24.07.2001	3.2	41.5	3.5	59.2	29.07.2001	5.7	73.4	4.3	71.3
25.07.2001	4.4	61.5	4.3	65.5	30.07.2001	5.8	82.8	1.5	64.5
26.07.2001	3.9	55.6	4.1	63.7	31.07.2001	4.8	63.1	2.0	60.9
27.07.2001	5.7	65.3	3.5	65.9	01.08.2001	5.3	75.4	3.2	-

Table 22: residence time of trajectories over Europe calculated in Arosa (arrival 6 UTC) and Jungfraujoch (arrival 8 UTC).

Meteorological conditions observed in this period can induce a transport of strong oxidised and polluted air masses from the polluted boundary layer to higher altitude. For example for the Mesolcina valley it was calculated that during one upwind phase the valley volume can be replaced up to five times (Furger *et al.*, 2000). On days with similar strong convective conditions as in the case described it was found that the pollutants from the boundary layer can reach altitude higher than 4 km (Nyeki et al., 2000). It is therefore plausible to think that after being transported up to higher altitude these strongly oxidised and polluted air masses can be transported over long distances possibly influencing more remote area. This dispersion towards more remote areas (in the free troposphere) is certainly favoured by sudden changes in the circulation as it occurred on the 30th.

In section 7.3.3 this case is discussed again with respect to the residence time analysis and ozone concentration in Arosa.

5.4.1.3 Correlation of trace gas measurements

Using all data from the 23rd to the 30th early morning (excluded morning measurement between 07 and 10 CET with village emission influence, see also 6.1.4) it was found that O_3 and NO_y and O_3 and CO respectively are strongly positively correlated (R^2 = 0.74 and 0.84). Such strong relationships are usually found for day time measurement at station in the boundary layer performed not to far away from emission sources (Cardenas *et al.*, 1998) and are mainly due to the fact that during day time in summer photochemical reactions convert NO_x to HNO_3 and PAN and simultaneously produce elevated ozone concentrations mainly through oxidation of reactive hydrocarbon and CO (section 2.1). For remote locations very strong relations are not expected due to different transport, formation and loss processes that undergo the different compounds (Zelweger *et al.*, 2000). No correlation was found e.g. under free tropospheric conditions between NO_y and CO (Wang *et al.*, 1996). The strong correlation found for this case suggests therefore that the influence of the boundary layer on trace gas in Arosa and at Jungfraujoch at the end of July 2001 was particularly strong. The correlations were very similar during day time and night time (Figure 56). Steeper slope could be interpreted as a stronger influence from the boundary layer. In this case the correlation between NO_y and ozone pointed to a stronger boundary layer influence in Arosa.

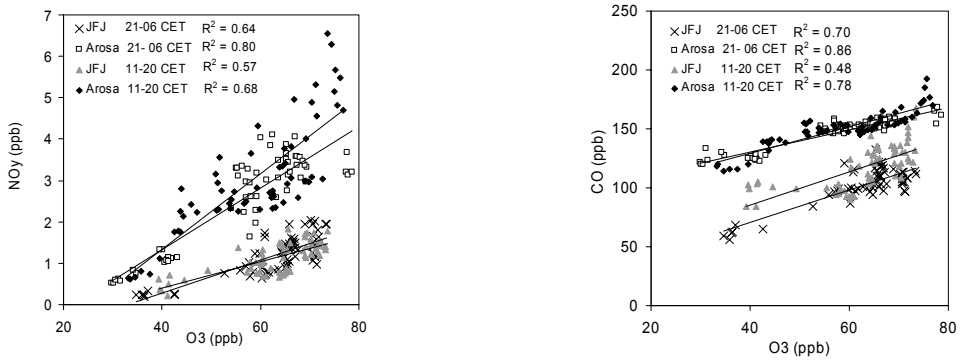


Figure 56: Scatter plots and correlation coefficients of observed hourly mean of NO_y versus O_3 and CO versus O_3 at Jungfraujoch and in Arosa for measurement between the 23rd and the 30th of July 2001. Night time and day time are separated. Measurements from 07 to 10 CET are excluded in Arosa.

5.4.2 The fronts of the 24th of June and 3rd of July 2002

In section 5.1.3 events of fronts occurring in the cold season were presented. Frontal passages however occur throughout the year. Figure 57 shows two front events occurred in summer (June and July 2002, the July case as part of the time series discussed in the section dedicated to the south foehn (5.3.2)). Both events were characterized by advective weather and low radiation and high humidity. In one case ozone concentration at Jungfraujoch was clearly affected by the passage. In the other case ozone at this high alpine station was not influenced. The most pronounced influenced were observed in Arosa; during the cold front passage ozone concentration in Arosa strongly decreased to concentration comparable to Chur at the mouth of the valley. This observation suggests that Arosa was directly affected by air uplifted from lower altitude. The strong increase in the ratio NO_x/NO_y depicted in Figure 57 (as a result of an increase in NO_x and a decrease in NO_y ,see for example Figure 41) further supports that fresh air was transported to Arosa after advection of well aged air masses. In the July event a clear motion from N NE strongly suggests

that this fresh air was advected from the Plessur valley (Figure 41). Despite the low value of residence time calculated for air masses arriving in Arosa (25th of June at 06 UTC: 3 days; 4th of July at 06 UTC: 1 day) the low ozone concentrations were on these days also influenced by advection of ozone titrated air from the (nocturnal) boundary layer. The low ozone concentration measured during this time can not be compared with the low ozone concentration found at the end of the July 2001 event described in the last section. On that event low ozone concentration were determined by transport, in these two front events ozone was the result of loss processes.

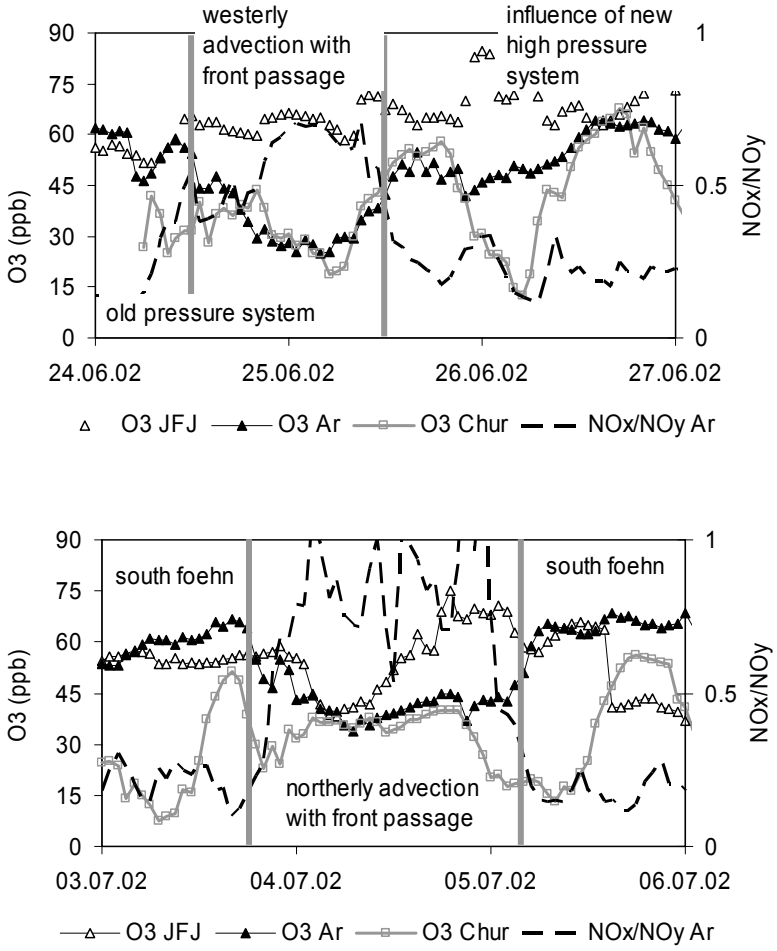


Figure 57: Time series of ozone, NO and NO_2 of the frontal passage on the 24th of June (top) and the 3rd of July (bottom) 2002. (ar= Arosa, JFJ= Jungfraujoch).

6 Weather classification and air pollutant concentration in Arosa

Chapter 5 reported case studies describing processes particularly important for ambient air concentration in Arosa. However a generalisation of these results is difficult to achieve. A method for daily synoptic weather classification in Switzerland was developed by Schüepp (Schüepp (1979), see also section 3.3). Nevertheless the application of such method for a direct comparison between the purposed weather types and air pollutant measurements in Arosa only allows describing some general tendencies. The classification is mainly based on the wind situation at 500 hPa and therefore only partially describes the air motion at lower altitudes. Slightly more valuable results can be found when Schüepp weather types are used to compare trace gas concentrations in Arosa with measurements performed at lower altitude (station Taenikon (538 m) in the Swiss Plateau). These results are described in Appendix A.1.

Section 6.1 applies a totally different approach for the description of the weather influence based on a daily classification that includes the local relative humidity. Differences in averaged diurnal variation of trace gases in Arosa allow the description of the influence of valley wind circulation, fronts and photochemical activity in a more general way. This analysis highlights the presence of local emissions throughout the year. The influence of the nearby village emissions is usually restricted to day-time. Comparison with trace gases diurnal variations at the NABEL stations Taenikon (538 m) and Jungfraujoch (3578 m) is of particular interest because there are no measurement sites other than Arosa situated at about 2000 m in the Swiss alpine area. According to this classification applied for Arosa measurements, section 6.3 presents the distinctly different influence of weather on trace gas concentrations at the three sites. Against all expectations before the campaign, the analysis shows that Arosa can not be considered as regularly and directly influenced by the free troposphere as the Jungfraujoch. Striking differences in trace gases concentrations between Arosa and Jungfraujoch are mostly found on summer nights during fair weather conditions suggesting advection from the (polluted) residual layer towards Arosa while the Jungfraujoch under similar condition is mainly influenced by free tropospheric air.

Section 6.4 presents correlations between trace gases using measurements performed in Arosa over a long period of time. Attention is focussed on the influence of different meteorological regimes on the correlations. Strong relationships are often found for day time measurements at stations located in the boundary layer (Parrish *et al.*, 1991). Such strong correlations might have several applications, for example, to compare the reliability of emissions inventory (Thielmann, 2000), to detect a special emission source (Cardenas *et al.* 1998) or to estimate the photochemical ozone production (Thielmann, 2000). In summer this correlation are caused by photochemical reactions leading to conversion of NO_x to HNO_3 and PAN, to production of ozone and to oxidation of reactive hydrocarbon and CO (section 2.1). Far away from pollutant sources such correlations are not expected due to different transport, formation and loss processes that the different compounds undergo (Zellweger *et al.*, 2000). No correlation was found for example between NO_y and CO under free tropospheric conditions (Wang et al., 1996). The analysis shows that trace

gases in Arosa correlate only weakly unless measurements on events with clearly similar transport conditions are considered (e.g. as in the case of south foehn).

6.1 Diurnal variation and local meteorology

6.1.1 Introduction

This section discusses the behaviour of O_3, NO_y and NO with respect to the local meteorological measurements. In case of "fair weather" conditions the ozone concentration was found to be rather high whereas lower concentrations were observed during "bad weather" conditions. This reflects the different balance between ozone production and ozone destruction processes occuring in the "air parcels" arriving at the measurement station. In order to better understand the variability of trace gases in Arosa their daily mean variation was calculated and classified into 4 different relative humidity classes. In addition, to take into account the seasonal variation of photochemical activity, the data set was divided into the 4 climatological seasons winter (DJF), spring (MAM), summer (JJA) and fall (SON). To define the 4 classes the 25% -, 50%-, 75% - percentiles of the daily mean of relative humidity were used (Table 23). Days with the lowest daily mean of relative humidity fell into class I, which correspond to days characterised by "fair weather" conditions while class IV contains days with the highest daily mean of relative humidity (most of the time characterised by precipitation (Table 24)).

RH (%)	Class I	Class II	Class III	Class IV
Winter	< 43.9 %	43.9 - 65.6 %	65.6 – 80.3 %	> 80.3 %
Spring	< 57.9 %	57.9 – 70.5 %	70.5 – 84.5 %	> 84.5 %
Summer	< 61.1 %	61.1 – 72.5 %	72.5 – 85.3 %	> 85.3 %
Fall	< 58.6 %	58.6 - 70.4 %	70.4 – 86.8 %	> 86.8 %

Table 23: 4 classes defined according to the 25% - , 50% - and 75% - percentiles of relative humidity (RH). Every season includes 6 months (corresponding to a 2 year data set).

# hours with r >0	Class I	Class II	Class III	Class IV
Winter	2 (1)	5 (2)	41 (8)	224 (21)
Spring	5 (4)	69 (19)	200 (35)	529 (41)
Summer	16 (8)	56 (15)	138 (28)	473 (44)
Fall	2 (1)	6 (2)	145 (20)	270 (22)

Table 24: Number of hours with measured precipitation intensity > 0 (mm/h) in each RH class and season. Brackets: numbers of days in which precipitation events occurred. In fall only 2001 precipitation data were available.

Table 25 shows the occurrence of weather types according to Schüepp (Shüepp, 1979; Wanner *et al.*, 1998) within the different RH – classes. Class I showed anticyclonic weather conditions as being predominant. This number decreased from class I to IV. In class III and IV the advective weather types North and West become more frequent. This is quite evident for North advection that always occurred with the highest frequency within class IV. The rather frequent convective weather type "indifferent" did not show such a clear tendency as the weather type "anticyclonic". In winter and spring a weak decrease from class I to IV was observed, whereas in summer and fall this weather type occurred more often within the less dry class III and class II. South advection was observed more often within class I and II (practically in all seasons), in agreement with south foehn yielding very often low relative humidity. The next four sections will present in more details the results for each of the seasons.

	RH	*E*	*S*	*W*	*N*	*C*	*I*	*H*	*M*
Winter	I	3	6	2	1	-	11	19	3
	II	2	10	8	3	1	11	6	3
	III	1	6	12	6	3	7	7	3
	IV	2	3	6	16	3	7	2	6
Spring	I	1	7	2	1	1	20	13	1
	II	2	6	5	1	3	17	7	3
	III	1	-	4	9	4	18	6	4
	IV	-	1	5	19	7	7	2	4
Summer	I	-	1	1	2	-	17	25	-
	II	-	4	1	1	-	24	15	2
	III	-	-	2	7	3	27	4	3
	IV	-	3	5	11	9	12	-	6
Fall	I	1	7	2	1	1	20	13	1
	II	-	10	2	1	5	28	11	8
	III	-	4	3	8	7	13	1	7
	IV	-	4	3	13	5	12	-	4

Table 25: Occurrence of different weather types (# days) according to Schüepp in the 4 different RH classes. E = east - advection, S = South - advection, W = west – advection, N =north – advection, C =cyclonic, I = indifferent, H = anticyclonic, M = mixed.

6.1.2 Winter

In winter the highest ozone concentration fall within class I (Figure 58). During class I days temperature remain stably above 0°C during several hours. The mean temperature difference between Arosa and Chur indicates that a temperature inversion separates the high mountain Arosa from Chur (Table 26, see also section 5.2). During these days wind speed values in Arosa also reach on average the lowest values (< 2 m/s during the whole day) indicating that the measurement station lies within a “calm”. This situation can be regarded as undisturbed from pollutants emitted in the plain.

The ozone maximum peak within class I is reached at early morning between 04 and 08 CET (i.e. at the end of the valley outflow period) and amounts to about 46 – 47 ppb. This situation is coincident with a minimum peak in NO_y which is about 1 ppb. Within class IV ozone concentration can reach an average of even more than 10 ppb lower than in class I. The largest difference in concentration is reached early in the morning. In the afternoon a weak increase in ozone concentration is observed (+ 3 ppb) leading to a second maximum peak. The weak temperature increase in the afternoon can probably be enough to sustain local mixing with air situated above the measurement station which is normally less influenced by deposition and titration. This maximum becomes less pronounced while shifting from class I to class IV and this is consistent with the local mixing hypothesis. The temperature difference between Arosa and Chur clearly indicates that no inversion layer is present between these locations within class IV. Such low and negative differences in temperature values between Arosa and Chur were found to be typical during periods influenced by a passage of a front connected with transport of ozone-poor air up to Arosa (section 5.1.3).

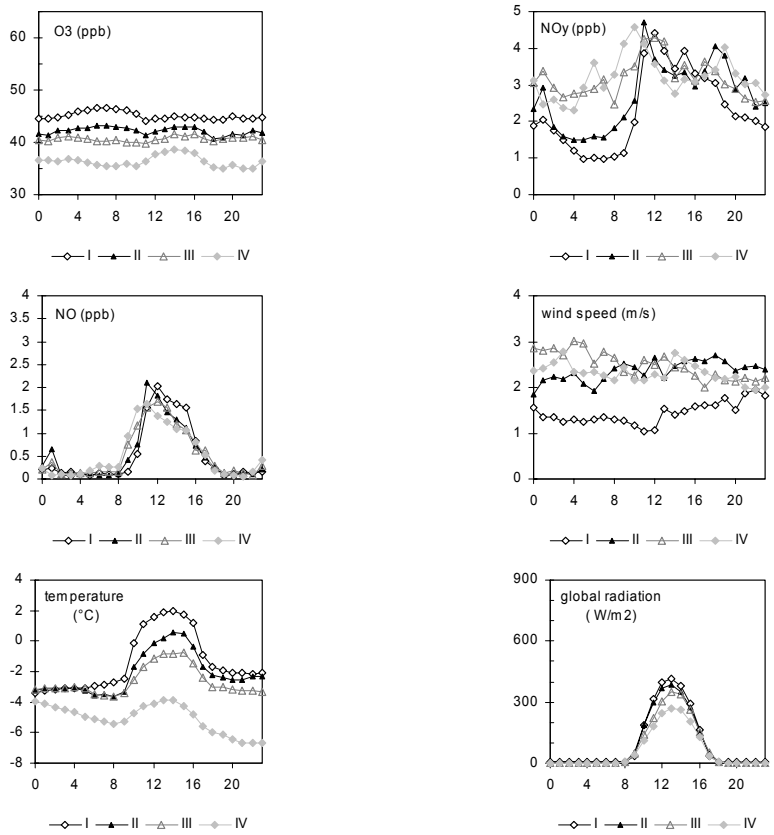


Figure 58: Daily mean variation of chemical and meteorological parameter in Arosa in winter.

The ozone concentration within class IV is thus mainly determined by advection of air from the boundary layer whose ozone content is depleted by deposition and titration with NO. The only moderate difference in NO_y between class IV and I also suggest that the lower ozone concentrations are not essentially due to titration occurring locally.

The NO daily variation clearly indicates that in winter and during day time the site is under considerable influence of local emissions. These concentrations are clearly independent on weather conditions and are not only a consequence of the nearby village emissions but also of the pollutants emitted near the measurement station and related to the ski activity. The concentrations observed during the maximum peak at noon are on average about 2 ppb independently of particular humidity class. As total reactive nitrogen also includes per definition NO, NO_y daily variation during day time shows a behaviour which is similar for each class. The most pronounced differences occur after midnight. Within class I and class II low concentrations are observed which also correspond to the daily minimum. This becomes most pronounced for class I. Within class III and class IV the concentration difference between day and night-time is not so pronounced and the diurnal variation becomes of much smaller entity.

Delta T (%)	Class I	Class II	Class III	Class IV
Mean between 10-15	-2.2 (4.5)	-5.0(3.8)	-6.3(3.0)	-7.7(2.9)

Table 26: Temperature difference between Arosa and Chur among the 4 relative RH classes in winter (for both locations hourly averages from 10 to 15 CET were used).

6.1.3 Spring

In spring the highest ozone concentration are again found within class I. The difference in the ozone concentration between class I and IV is more pronounced than in winter, reaches about 15 -17 ppb and can be explained by the strong increase in photochemical activity during fair weather conditions occurring in spring (Carpenter *et al.*, 2000).

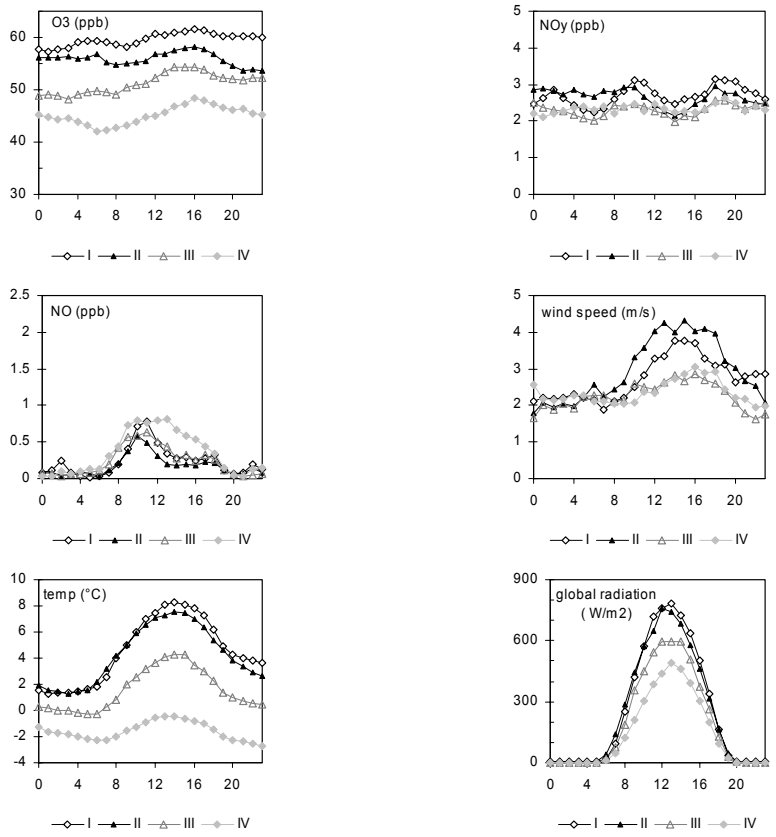


Figure 59: Daily mean variation of chemical and meteorological parameter in Arosa in spring.

The daily variation in wind speed shows that the valley wind circulation already fully develops during spring time, this is most pronounced in class I and class II where the incoming solar radiation almost reaches typical summer values. This air motion through the valley is expected to generate transport of ozone precursors up to Arosa (Prevot et al., 1993; Vergeiner & Dreiseitl, 1987). Indeed ozone concentration reaches its maximum in the afternoon, which provides evidence for photochemical activity in Arosa at least in the classes I and II. The afternoon slight increase in ozone within class IV is most probably due to local mixing as previously described for the diurnal winter time. The NO daily variation is again rather independent of the weather conditions. The maximum concentrations clearly indicate that the local emissions have decreased since winter; the ski season usually ending between February and March. The peak is, compared to winter time, shifted to the morning hours and corresponds to the onset of the slope wind transporting emissions from the nearby village up to the station. NO_y does not show significant difference among all 4 classes. A comparison with the winter data shows that the night concentration has clearly increased and a night minimum has disappeared (class II) or is not detectable any longer (class I). The fact that the local emissions contribution is less pronounced

in spring than in winter implies that NO_y better reflects transport from a source area situated far away from the measurement station. The NO_y spring measurements show slightly higher values for good weather conditions than for bad weather conditions. This could be related to the enhanced atmospheric instability during fair weather which is already observed in spring (Seibert et al., 1998) and clearly characterises the summer. The temperature difference between Arosa and Chur shows that a very stable temperature inversion which lasts the whole day is not a climatological spring feature (Table 27).

Delta T (%)	Class I	Class II	Class III	Class IV
Mean between 10-15	-8.9 (2.6)	-9.1 (2.6)	-9.4 (2.5)	-8.9 (2.6)

Table 27: Temperature difference between Arosa and Chur in spring in the 4 relative humidity classes.

6.1.4 Summer

During the summer months the most striking feature is the occurrence of the ozone maximum at night after sunset (Figure 60). Ozone decreases shortly after sunrise when the up slope wind sets in and can be explained by the advection of air that during the previous night descended the valley; thus more subjected to dry deposition. In addition the low ozone concentrations in the morning time could partly be attributed to titration with NO from the local emission. Indeed assuming a mean up slope wind speed of about 2 m/s, the air from the village reaches the measurement station in 7 – 14 min depending on the wind direction. This rough estimate indicates that emissions from the village can reach the measurement station in few minutes after the start of the up slope wind.

The differences in ozone concentration between class I and class IV range between 9 and 15 ppb and become sharper in the late afternoon. The NO daily variation shows once again the influence of local emissions during morning time. The NO concentrations observed are independent of the weather and reach their lowest level compared with other season. The differences in NO_y concentration among the 4 classes become more evident in summer than in spring. Fair weather conditions are clearly associated with higher NO_y concentrations in Arosa. During these days the high solar radiation induces a more efficient vertical transport as shown by the high wind speed values. Furthermore a higher photochemical activity leads to an enhanced oxidation of ozone precursors (section 2.1). Within class I and II the highest NO_y concentrations (except for the morning peak) are observed in the late afternoon and at night. A similar and even more pronounced behaviour is found for the CO concentrations (Figure 58). This information, combined with the ozone maximum occurring at night, clearly shows that photochemically well processed air reached the measurement station at night.

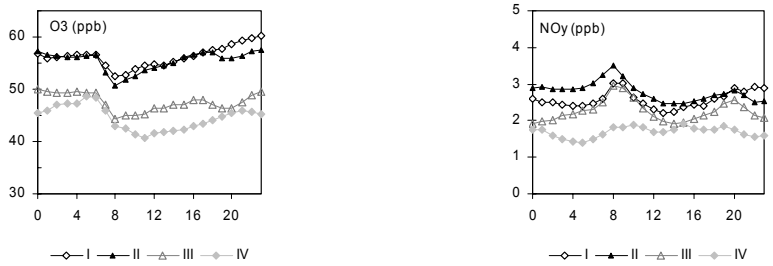


Figure 60: legend see next page

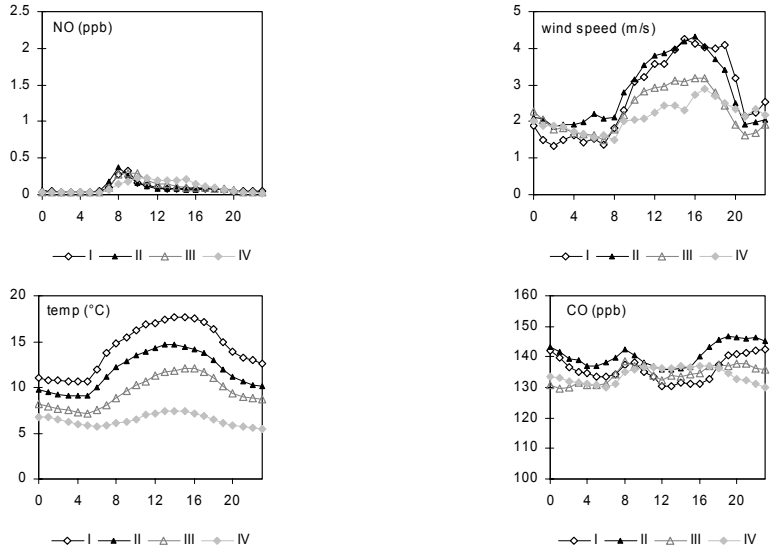


Figure 60: Daily mean variation of chemical and meteorological parameter in Arosa in summer.

6.1.5 Fall

Ozone in fall shows generally the lowest values throughout the whole year (Table 9). The daily variation of ozone resembles the winter variation. The temperature difference between Arosa and Chur shows that strong inversion layer can already decouple the high mountain station from the plain station (Table 28). The differences in ozone between class IV and class I are in the order of 8 – 11 ppb (Figure 61). As the contribution of photochemical activity during fair weather conditions at fall is decreasing (Jacob *et al.*, 1995), loss processes such deposition and titration determines ozone concentration similarly as in winter. NO_y as well follows a similar trend as in winter but with a small diurnal variation and a minimum (< 1 ppb on average) after midnight (most pronounced within class I). The CO data shows a similar behavior as NO_y. Compared to the summer values concentrations of carbon monoxide are much higher. This result can be explained by the general seasonal variation of carbon monoxide (section 4.5). This behaviour is more striking within class IV. This fact can be connected to fronts and advective weather and therefore to enhanced transport from the polluted boundary layer. Within class I carbon monoxide clearly shows a diurnal variation reaching a night a minimum around 130 ppb early morning.

NO measurements suggest that the local emissions are not as large as in winter yet. Compared to summer, the wind speed measurements show that the wind valley circulation less develop mainly due to the reduced values of incoming solar radiation.

Delta T (%)	Class I	Class II	Class III	Class IV
Mean between 10-15	-2.1 (4.7)	-5.0 (3.7)	-7.5 (2.5)	-8.9 (2.3)

Table 28: Temperature difference between Arosa and Chur in fall in the 4 relative humidity classes.

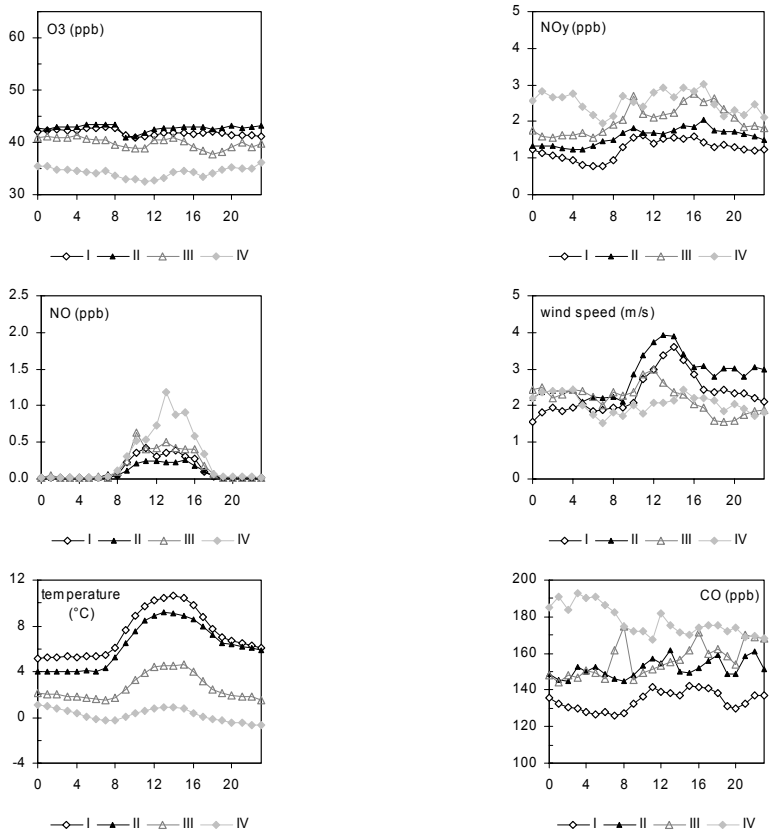


Figure 61: Daily mean variation of chemical and meteorological parameter in Arosa in fall.

6.2 Time of ozone maxima

In section 6.1 it was found that the time of the ozone maxima in the mean diurnal variation differed in a seasonal fashion. The next figure outlines at which time of the day the daily ozone maximum occurs (Figure 62). The ozone maximum of each day was determined together with its occurrence time. For example in the 154 days corresponding to winter time, the ozone maximum occurred in 5.8% of the days (9 days) between 00 and 01 CET at night.

In summer the daily maximum usually occurs after sunset and before sunrise. The absence of an ozone maximum in the morning time can be expected, when the upslope wind transports ozone-poor air from the valley floor and local emissions from the village to the station. A daily ozone maximum occurred during daytime (between 07 and 20 CET) only during 18.5% of the days. The remaining fraction originated in the absence of solar radiation and can therefore not be explained by the local photochemical production. These peaks at night are most of the time supposed to be caused by transport of photochemically well processed and ozone-rich air from distant location.

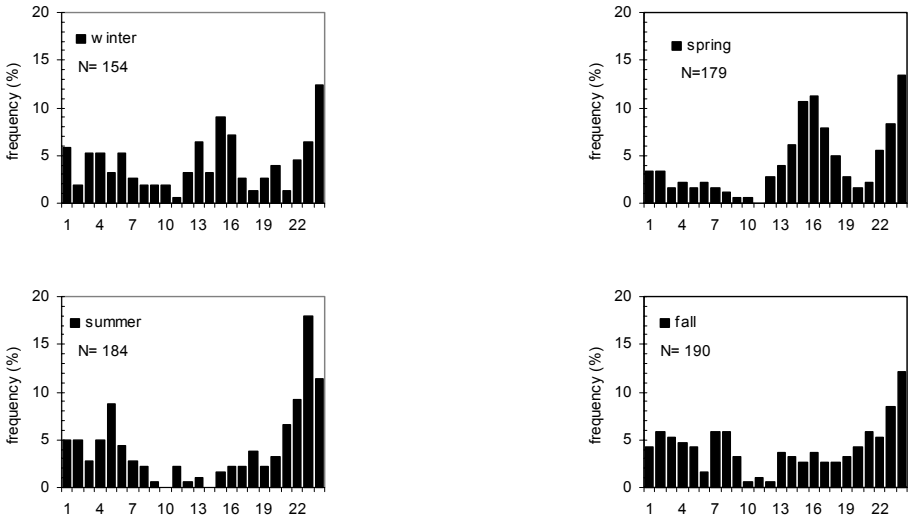


Figure 62: Time occurrence of ozone maxima in Arosa (N is the number of days with measurement within each season). X-axis = hours of the day.

To further investigate the origin of air masses in summer nights (from 21 to 06 CET) wind direction measurements at Weissfluhjoch (2690 m) are taken in consideration. Figure 63 (left) shows that during these summer nights most of the times wind measurement at Weissfluhjoch was indicating North direction (54 % range: 315° – 44°). During 26 % of the nights wind was coming from the South sector (range: 135°-224°). Less frequent was wind from the West direction (18%) and from the East direction (2 %).

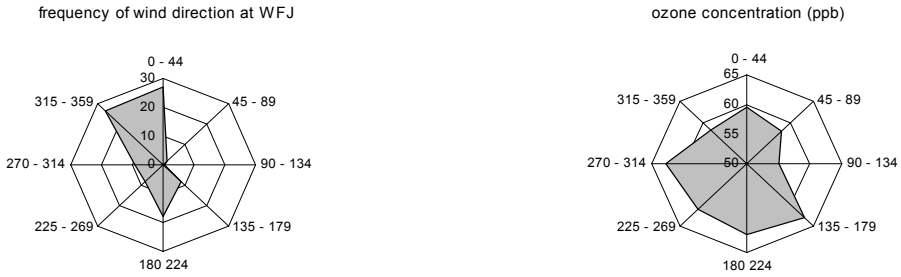


Figure 63: Occurrence (in %) of nightly ozone maximum in summer and relation with wind direction measured at Weissfluhjoch (left) and mean value of ozone maximum and relation with wind direction measured at Weissfluhjoch (right).

Figure 63 (right) shows that whenever wind at Weissfluhjoch was coming from the South the ozone maximum were on average slightly higher (63.0 ppb) than during the more frequent northerly advection (58.7 ppb). The ozone maxima in Arosa do not denote a remarkable daily variation along the different seasons (Figure 64, left). In fall and winter daily maxima are on average around 45 ppb whereas in summer and spring they are around 60 ppb. A weak tendency showing higher ozone maxima in summer nights in case of fair weather days is observed (Figure 64).

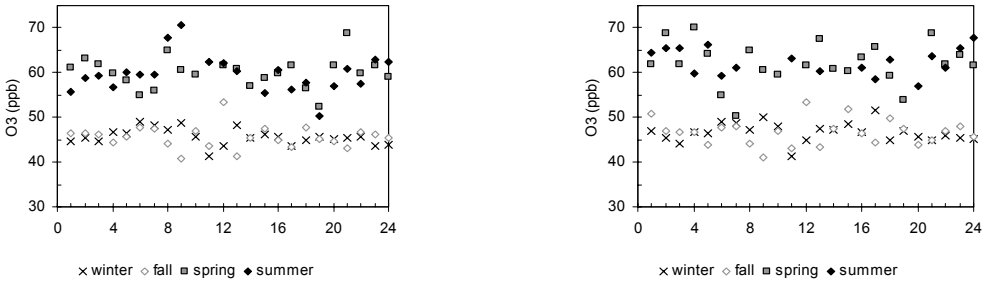


Figure 64: Ozone maximum in Arosa do not denote a particular daily variation along the different seasons. Left: entire data set, right selected days with fair weather conditions (daily average of relative humidity <80%).

Also in spring the photochemical activity plays an important role. Compared to summer a significant amount of spring daily maximum (48%) is concentrated in the afternoon hours between 12 and 18 CET. A substantial amount of these afternoon peaks could be explained by local photochemical events. The role of local photochemical ozone production in the transition from winter to summer is even more evident if the time occurrence of the maximum is considered on a monthly basis (Figure 65).

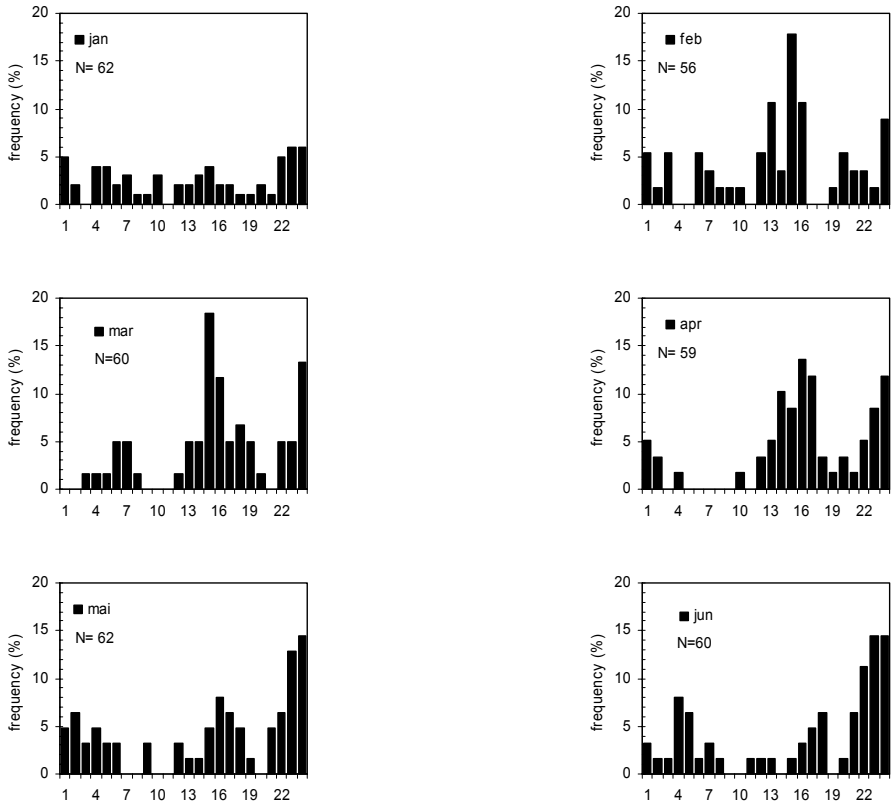


Figure 65: Same figure than in Figure 62. Here a monthly basis resolution is considered. Data from January to June.

Towards the end of winter photochemical processes become suddenly more important (Carpenter *et al.*, 2000), this is pronounced at high altitude above the

inversion layer and can be explained by the increasing values of solar radiation whereas at low altitude (e.g. on the Swiss Plateau) ozone production is still inhibited by a pool of cold and NO_x rich air (Bronnimann, 1999). Starting from March/April, when surface radiation becomes higher, mixing is more efficient and stagnant cold air is less frequent. Ozone production can occur under these conditions also at lower altitude (Bronnimann, 1999).

The observation made in Arosa from February to May with a large amount of ozone maximal peak occurring in the afternoon could be explained by the combination of different factors: 1) increasing solar radiation value at high altitude stimulate local ozone production, 2) in the plume of large agglomerations photochemical ozone production has not reached its maximum yet, 3) convection leading to vertical transport over the plain regions is not as developed as in summer.

The finding that a consistent amount of ozone maxima is found during day time indirectly suggests the importance of photochemical activity for the spring ozone maximum.

6.3 Comparison Arosa and NABEL stations Taenikon and Jungfraujoch

This section compared trace gas diurnal variations in Arosa with the variations at lower altitude station as Taenikon and at higher alpine Jungfraujoch. In the last section Arosa measurements were grouped and presented according to relative humidity classes. To classify the measurements performed at Taenikon (Figure 66) and at Jungfraujoch (Figure 67) the same relative humidity classes were applied. This means that the same days included in a specific class in Arosa are used to classify the measurements at Taenikon and at Jungfraujoch.

In winter time the highest NO_x concentrations at Taenikon (21.5 ppb as daily average) are clearly reached within class I (fair weather) showing frequent inversions (Figure 66). Thus this occurs thus when NO_y concentrations reach the lowest values in Arosa (at night time). The lowest NO_x concentrations at Taenikon (11.8 ppb as daily average) are reached instead when in Arosa the weather conditions were deteriorating (class IV). The strong temperature inversion between Chur and Arosa for days within class I is representative for a strong inversion layer located over a large part of the Swiss Plateau. The relevance of these strong inversion layer episodes gets even stronger while considering the ozone concentration.

The increase in NO_x concentration in the morning and in the evening at Taenikon correlates with the presence of emissions associated with the morning and evening traffic. The ozone concentration increase in Taenikon during afternoon time reminds of the increase observed in Arosa during bad weather and can also be probably explained by a vertical air mixing.

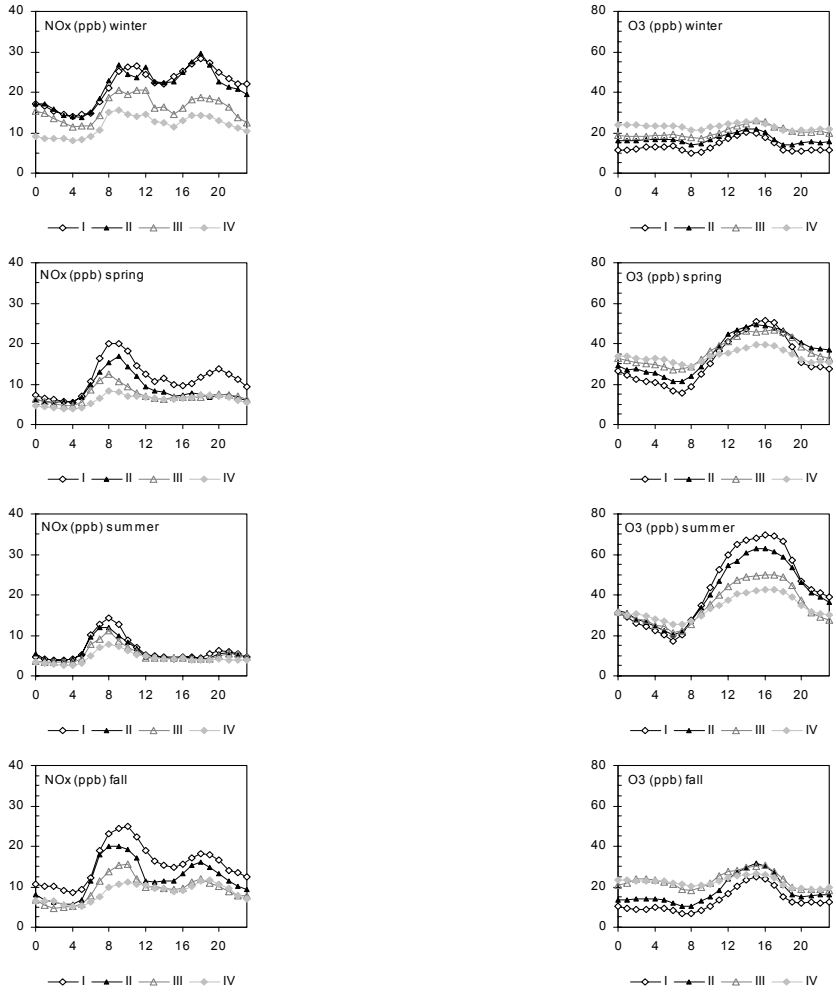


Figure 66: NO_y and O_3 diurnal variation in Taenikon (540 m) for the relative humidity class I to IV as defined for Arosa along the 4 season.

The Jungfraujoch winter data show the same general tendencies as those calculated for Arosa (Figure 67). Both stations are in fact located above the inversion layers when inversion occurs. At this much higher alpine station the local emission can be regarded as negligible (Forrer *et al.*, 2000). Biggest differences are encountered between the different RH classes. Similarly to Arosa the lowest values in NO_y are reached within class I (0.37 ppb as daily average) whereas the highest value are reached within class IV (0.77 ppb as daily average). Considering the lowest mean value reached in Arosa at night time during fair weather (1 ppb NO_y in Figure 58) it can be seen that the cleanest air masses in Arosa still have higher NO_y content than the most polluted air masses at Jungfraujoch. Zellweger *et al.* (2002) found for undisturbed free troposphere conditions at Jungfraujoch a mean NO_y concentration of 0.5 ppb whereas during disturbed free troposphere conditions NO_y reached 1.2 ppb. This result suggests that Arosa even during the cleanest days (class I), can not be considered as a site regularly exposed to the free troposphere.

The difference in ozone concentration at Jungfraujoch between the 4 classes is less pronounced than in Arosa and practically no diurnal variation is detectable. Compared to Arosa the smallest difference in ozone is found within class I (Jungfraujoch: 47.3 ppb, Arosa: 45.2 ppb as daily average) whereas the largest difference is found within class IV (Jungfraujoch: 45.1 ppb, Arosa: 36.4 ppb). This

provides evidence that Arosa is more exposed to ozone loss during bad weather than Jungfraujoch is (north and westerly advection according to Table 25, see also section 5.1.2.2). Obviously ozone-poor air from the boundary layer can reach Arosa much easier than the 1500 m higher located Jungfraujoch.

In the warmer seasons (spring and summer) the effect of photochemical activity gets evident. Compared to wintertime all three stations show higher ozone concentration for each class. Taenikon clearly shows a maximum in the afternoon and a minimum at night (Figure 66). This is most pronounced during fair weather conditions and typical for the (rural) boundary layer (2.3.1). NO_x concentrations at Taenikon in spring and summer still show two peaks one in the morning and one in the late afternoon, but the concentrations clearly reached lower absolute values relative to winter-time as a result of enhanced mixing and dilution.

At Jungfraujoch an evident diurnal variation in ozone is not observed in agreement with Zellweger *et al.* 2002. The differences between each class are also definitely smaller than in Arosa or Taenikon (Figure 67). In the afternoon during summer days with fair weather conditions (class I) ozone concentration at Taenikon reaches on average 70 ppb whereas in Arosa and Jungfraujoch ozone is on average only around 60 ppb. This indicates that the "normal" ozone vertical distribution can be temporarily altered by fair weather conditions (mainly class I). The NO_y and CO diurnal variation at Jungfraujoch shows for class I and II a maximum peak in the afternoon Figure 67 and Figure 68). This is most striking in summer and spring. A similar behaviour was reported also for CO (Forrer *et al.* 2000) however without any separation in classes. Lugauer *et al.* (1998) found a similar diurnal variation in the warm season at Jungfraujoch for aerosol; this became most evident during anticyclonic weather conditions. Airborne lidar measurements revealed that in summer pollutants from the boundary layer can reach an altitude of 4.2 km in the Jungfraujoch region (Nyeki *et al.*, 2000).

Zellweger *et al.* (2000) attributes the NO_y increase in the afternoon, found in single events, to vertical transport of photochemically well aged pollutants from the Swiss Plateau. At night the minimum in NO_y and CO indicate that cleaner air possibly influenced by the free troposphere, is advected to the measurement station at Jungfraujoch (Figure 67). This was suggested first by analysing Jungfraujoch aerosol measurements that revealed a free troposphere influence in the diurnal period 03 – 09 CET (Nyeki *et al.*, 1998). The advection of cleaner air at night during fair weather was found not to happen in single cases when a very stagnant situation with weak and undirected wind was observed at 500 hPa (Zellweger *et al.* 2000).

In contrast to what seen for Jungfraujoch a different diurnal variation in NO_y and carbon monoxide is observed in Arosa (note the different axes compared with Jungfraujoch) (Figure 60). Here higher concentrations are found during fair weather days through the entire day whereas at Jungfraujoch this happens only after about 15 CET. From this time pollutants reach by thermally driven convection the high alpine station. From this comparison and the conclusion in section 6.1.4 about the ozone maxima found after sunset we can conclude that Arosa is most of the time influenced by the boundary layer during summer. During day time there is a direct influence during the up slope winds phase while at night time the influence come from the residual layer. This is further supported by a comparison with Lugauer & Winkler (2002) who analysed trace gas concentrations at the pre-alpine station Hohenpeissenberg (985 m, located 60 km SW from Munich, at night above the

nocturnal inversion layer) finding a similar NO_x diurnal variation on fair weather days (between ~ 1 and 2 ppb) as NO_y in Arosa.

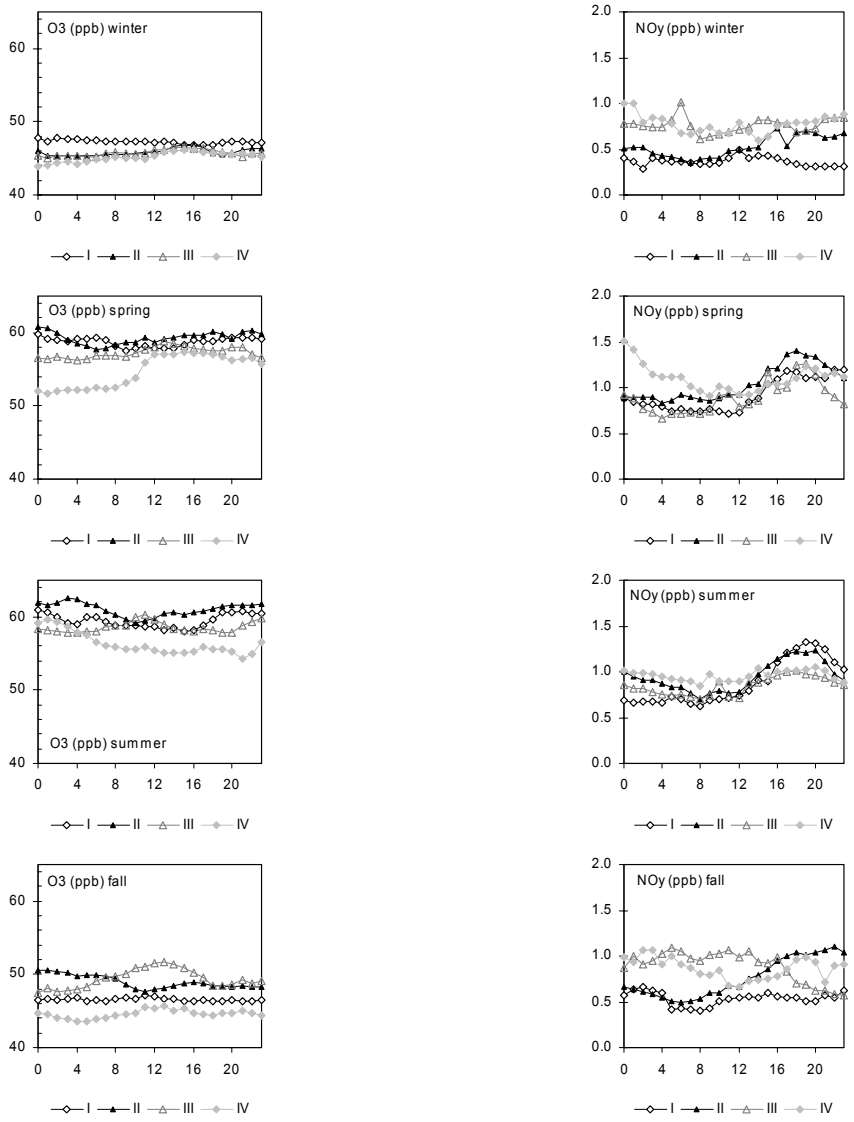


Figure 67: NO_x and O_3 diurnal variation at Jungfraujoch (3580 m) for the relative humidity class I to IV defined for Arosa.

Figure 68: CO diurnal variation in summer and fall at Jungfraujoch for the relative humidity class I to IV defined for Arosa.

In fall Taenikon exhibits similar variation like in winter, both for ozone and NO_x. Similarly to winter the reversal behaviour in ozone and NO_y in the different classes

observed in Arosa provide evidence that temperature difference between Arosa and Chur (Table 28) is representative for a region including a large part of the Swiss Plateau.

A similar behavior as in winter is observed in fall at Jungfraujoch as well (Figure 67 and Figure 68). It was already observed that days within class I are not associated with the highest ozone concentrations. This observation can be explained by the temporal distribution of the days within class I, II and III. Indeed 63 % are found in the second part of the season where intensity of photochemical activity has already decreased compared to September. On the other hand a reversal tendency was found within class II and III in which 56 % of the days were found in both classes in the first half of the season.

6.4 Relation between trace gases

In single cases presented in sections 5.1.3 and 5.4.1 strong correlations were observed among different trace gas. The relationship between the measured trace gases was investigated for November and December 2001 (winter) and June, July and August 2002 (summer) in which the entire dataset was available. The main interest is to see if there are substantial differences in the correlations within these 2 groups. Again daily means of relative humidity were considered in order to discriminate among days with similar weather conditions. Data contained in each class were additionally subdivided into day time and night time.

Figure 69 shows the relationships between O_3, CO, NO_y and NO_x during winter time for the night time. For better comprehensibility the figure shows only data within class I (days with the lowest daily mean of relative humidity, < 25% -percentile) and class IV (days with the highest daily mean of relative humidity, > 75% -percentile). The negative slopes between O_3 and pollutants CO and NO_y in each group suggest that O_3 in Arosa is mainly determined by the strength of O_3 loss processes. The very strong correlations found in class IV were driven by the single event registered in November 2001 and described in section 5.1.4. This gets evident if one considers that, during this event, CO concentration remained > 200 ppb, NO_y > 8 ppb and O_3 < 20 ppb during several hours. However no NO_x was measured during this event and this makes the correlation possibly more representative for the entire period. As soon as NO_x raises O_3 decreases. Note that similar trend between NO_x and O_3 is also found for day time and within both classes IV and I. This can be explained by a reduced photochemical activity in winter. NO_2 can dissociate also in winter, however no net O_3 production is expected since the scarce incoming solar radiation in winter time is not sufficient to sustain the important OH-radical production, which is limiting for high ozone production (section 2.1). However different studies postulated that a weak ozone production even in the cold can not be excluded a priori (Huntrieser *et al.* 2002; Li et al. 2003; Bronnimann and Neu, 1998).

The correlation between CO and NO_y is clearly a positive one. The result is again more evident for class IV and strongly determined by the pollution event mentioned above. Separation between data at night-time and at day-time does not produce significant differences in the slope (not shown).

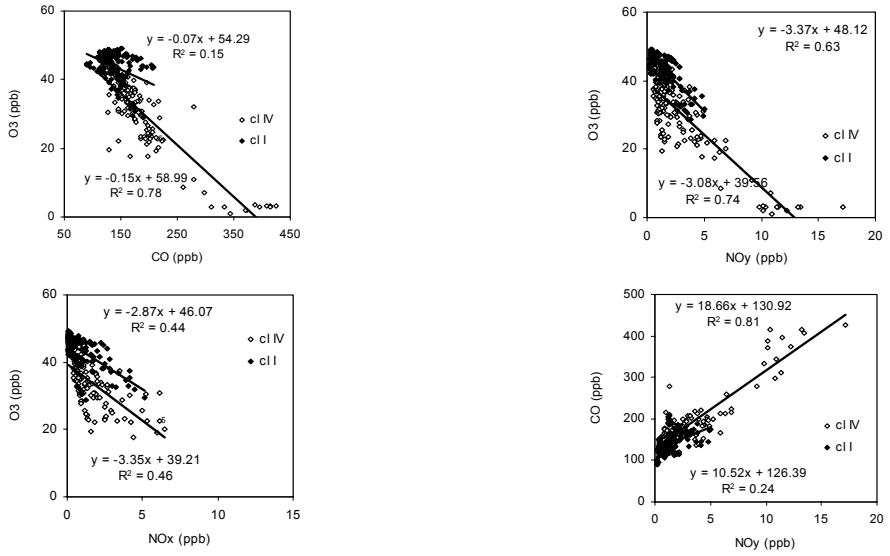


Figure 69: Correlation between different trace gases measured in Arosa in winter (night time between 19 and 06 CET). Class I : days with the lowest daily mean of relative humidity (< 25% -percentile). Class IV : days with the highest daily mean of relative humidity, (< 75% -percentile).

Figure 70 shows the same kind of relationships calculated for summer (day-time). The strong photochemical ozone production occurring during this period of the year constitutes an additional process to consider while interpreting these plots. The correlations were found to be generally weak showing only tendencies. The results show that within class I the relation between ozone and CO and between ozone and N - species has turned positive, whereas in class IV (day-time) photochemical ozone production could be limited by the much reduced solar radiation. This is supported by the absence of correlation between ozone, NO_y and CO.

CO and NO_y are positively related and within class I this relation is even better than within class IV. Enhanced NO_y loss during bad weather (section 2.2) can provide a plausible explanation. Indeed the HNO_3 amount in NO_y is larger during summer due to photochemical activity. Since HNO_3 can be more easily washed out compared to other NO_y species, the bad correlation within class IV is most probable the result of HNO_3 removal.

A positive correlation between ozone and NO_z is expected in case elevated levels of ozone and NO_z were a result of high photochemical activity. Th slope of such correlation could be regarded as the number of ozone molecules produced per molecules of NO_x consumed (Olszyna *et al.* (1994)).

Similarly to what observed for NO_y and ozone no significant correlation is found in class IV, whereas a positive tendency is found in class I. Such flat slopes were found in summer for VOC sensitive air parcel in which ozone production is less efficient. It is important to point out that a fair comparison of these slopes would need substantial better correlation (Thielmann, 2000). Moreover such flat comparisons were determined for single (short) events whereby Figure 70 reports data from three months long measurements (in class I). In the single event described in section 5.4 the ratio $\Delta O_3/\Delta NO_y$ amounts for the day time period to 10.8 by a substantial stronger correlation (R^2=0.75, note that measurement of the 24th were not considered to calculate this slope as influenced by weak perturbance) which is representative for

air parcels in which ozone production is determined by the availability of NO_x (Thielmann, 2000).

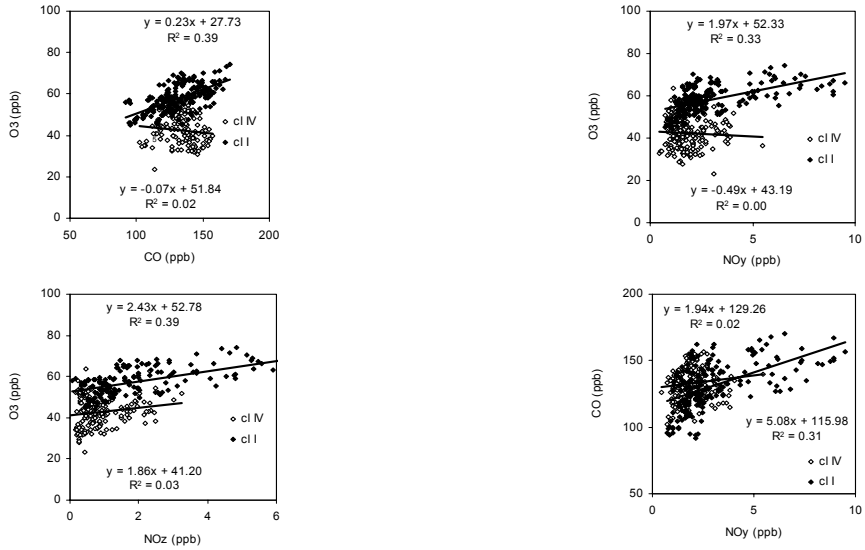


Figure 70: Correlation between the different trace gases measured in Arosa in summer (day time between 11 and 19 CET).

Despite the separation into classes with similar (local) meteorological condition the correlations in Figure 69 and Figure 70 remained weak. Reasons leading to such a weak correlation faraway from sources were already discussed in 5.4.1.3. In addition to weather conditions it is important that the flow pattern of the air parcel arriving in Arosa remain similar during the period for which the correlation is investigated. In such case one might expect that the different production and removal processes remain constant and that the different behavior of the pollutants with respect to these processes remain also constant. Zellweger *et al.* (2000) did not found simple correlations between trace gases in summer, however in cases of thermally driven convection (i.e. days characterized by afternoon vertical transport of pollutants from the boundary layer) a positive correlation between NO_y and CO was found. Figure 46 shows the relationship of NO_y with ozone for the foehn events (selected according to procedure in section 5.3.3). The backward trajectories for those event depicted in Figure 42 are suggesting a similar flow pattern bringing air parcel to Arosa. Considering that the measurements are distributed on foehn days over 2 years the correlation are remarkable and suggest the importance of constant flow conditions while analyzing such correlations between trace gases.

In section 6.1 it was observed that early in the morning (between about 03 and 06 CET) the measurement station in Arosa was not influenced by local emission. For this morning time the ratio NO_x/NO_y and NO_y/CO was separated according to the relative humidity classes I to IV (described in section 6.1). Both ratios reflect the aging process occurring in an air parcel. NO_x/CO averages near a source (e.g. in a city center) about 0.1 (which is valid also for NO_y/CO as NOy close to the source is practically equal to NO_x). The ratio NO_x/NO_y in fresh air is close to 1 and gradually decreases with increasing degree of NO_x oxidation (Hering *et al.* 1998). In region remote from emissions the interpretation of this ratio becomes difficult. Indeed the NO_x/NO_y accounts only for dilution effects whereas the NO_y/CO also accounts for deposition effects (Zellweger *et al.* 2000).

Figure 71 shows that two different general trends for NO_x/NO_y and NO_y/CO can be found while comparing winter to summer. The lowest mean NO_x/NO_y (0.37) occurred within fairest days of class I in winter. This value was also associated with the highest ozone mean value (Table 29). Most of the times these days were found during anticyclonic weather conditions. Moving towards the more humid classes II, III and IV, an increase in the mean NO_x/NO_y was found (cl II: 0.52, cl III: 0.60, cl IV: 0.67). Simultaneously these ratios became associated with decreasing mean ozone concentration which is explained by enhanced contribution of fresh and ozone poor air from lower altitude during advective weather. The changes in the ratio NO_y/CO is less evident but consistent with the changes in the ratio NO_x/NO_y. Moving from class I to class IV the ratio NO_y/CO increases.

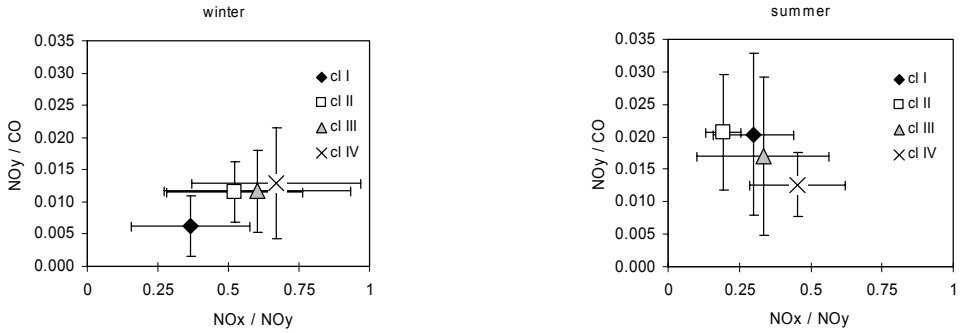


Figure 71: NO_y/CO and NO_x/NO_y during summer (June, July and August 2002) and winter (November and December 2001), only for early morning data (03 – 06 CET).

In summer morning time the NO_y/CO decreased on average with the deteriorating of the weather conditions. This is explained by enhanced wash out of NO_y species. Simultaneously NO_x/NO_y increased as NO_y mainly consists of not strongly oxidized nitrogen species. Standard deviations within each class were even larger than in winter. Note however that within class I and class II the NO_x/NO_y ratio only slightly varied as compared to the large variation of NO_y/CO. This can be understood as NO_x/NO_y certainly better indicates the presence of fresh emission. The values are clearly lower than 0.4 (suggested by Olszyna *et al.* (1994) for strongly oxidized air in summer) and the small deviations confirm that during fair weather days fresh emission did not reach the station at night. The larger deviation of NO_y/CO stands for the variability in the air masses advected at night to the station. The low ratios within class I and II are clearly associated with higher ozone concentrations (Table 29). This can be regarded as the result of strong photochemical production.

For the above mentioned foehn events in summer a NO_y/CO of 0.021±0.007 was found. This value is similar to the value found for class I and class II. This again indicates that during foehn cases air advected from the Po basin is photochemically well aged (in summer).

O3	Winter		Summer	
(ppb)	Mean	st.dev	Mean	st.dev
Cl I	44.1	4.3	57.5	8.0
Cl II	39.1	4.9	54.6	7.4
Cl III	37.9	4.12	47.3	8.9
Cl IV	30.7	12.1	47.5	9.1

Table 29: Averaged ozone concentration and standard deviation in each relative humidity class I to IV. This table contains data relative only for early morning measurements (03 – 06 CET).

7 Ozone in Arosa and trajectory analysis

Possibly the most significant caveat of the methods used in chapter 6 is the lack in the explicit description of the history of the air parcels. Trajectories can be used to overcome this problem (Stohl, 1998).

In section 7.1 the residence time analysis developed by Pochanart *et al*. (2001) is applied to measurements performed in Arosa. A closer analysis of this method reveals its limitations. Correlation between ozone in Arosa and residence time over Europe of air parcel arriving in Arosa is weak even in the photochemically more active warm season (section 7.1). Results do not speak in favour of any simple and strong correlation between both quantities. The residence time is potentially an estimate of the contact time of air parcels with European emission but it does not consider other aspects as for example the presence of strongly polluted area within the continent or the weather situation along the air parcel path (7.2). The approach is also not completely adequate to obtain ozone background values by extrapolating to zero days residence time. Indeed low ozone concentrations in Arosa are often associated with the passage of frontal systems also in summer, i.e. uplifting of an air mixture containing also air more subjected to ozone loss processes (section 7.3.1).

The results show that synoptic weather influences this relationship (section 7.3.1). In case of south foehn cases residence time and ozone are shown to be independent. This result identifies once again the Po basin as an important pollutants source (section 7.3.2). Air parcels which experienced a northerly advection or very moist weather also show no dependence of ozone on residence time. A strong correlation between ozone and residence time is observed in June and July during days characterized by anticyclonic conditions. These fair weather events occur as long episodes outgoing from typically bad weather situations with a day after day increase in ozone in Arosa. Two of these events are studied in more details (7.3.3) and they confirm again the importance of weather conditions and of the spatial distribution of emissions within Europe for ozone concentration in Arosa.

An agreement with the results presented in the study of Pochanart *et al*. (2001) is achieved when measurements within the months are averaged over many individual cases by their categorization into different residence time classes (section 7.1). The concept of the procedure proposed by Pochanart *et al.* (2001) is simple. Using two different approaches the concept of this analysis is extended to air parcels that experienced fair weather conditions along their travel towards Arosa, i.e. most favorable conditions for photochemical production. In the first approach, based on local relative humidity, a positive correlation is obtained from May to July but not in August (section 7.3.4). In the second approach the solar radiation along the trajectories is approximated by ECMWF radiation fields (section 7.3.5). Monotonically decreasing ozone concentrations are found starting from days with highest radiation along the trajectories to days showing the highest sky coverage. The residence time analysis yields a positive relationship between residence time and ozone during fair weather days.

7.1 Correlations between residence time over Europe and ozone

Residence times of air parcels over Europe were calculated from ECMWF-backward trajectories ending every day in Arosa at 06 UTC using the method described in section 3.4.3. Averaged ozone concentrations measured from 03 to 06 CET were matched with the corresponding residence times. Figure 72 shows the relationships between ozone measured in Arosa and the residence time of air parcels over Europe for the different twelve months for 2 years. Every single day within one month is represented by a point. The correlation coefficient R^2 is generally lower than 0.4 (Table 30). In some months (9 out of 24) the slopes are significantly different from the null - hypothesis (gray area in Table 30, p-value < 0.1, obtained with t-test analysis with a confidence interval of 0.01) but only for June and September the relationship between ozone and residence time is found to be significant for both measurements years. In the remaining cases significant correlations are found for a given month within one year only, but they can not be confirmed within the other year (e.g. for August the slope is significant in 2001 but clearly not significant in 2002).

Months belonging to the cold season (from October to February) are not characterized by a significant correlation. The sunlight intensity is obviously too low to sustain a relevant ozone production all over Europe. The months which show a slightly positive correlation between ozone and residence time are mainly those belonging to the warm season (from March to September) which is compatible with an increased photochemical ozone production on this months. According to Pochanart *et al.* (2001) who developed this method (section 2.3.4) this result can be explained as follows: with every additional day residence time over Europe air parcels come in contact with an increasing amount of ozone precursors and accumulate ozone along their path towards the Alpine region. Data presented in Figure 72 together with the correlation coefficients described above (Table 30) show that, however, the tendency to accumulate ozone is not very pronounced. In May, for example, the correlation between ozone concentration and residence time is generally very poor. In this particular month a group of days show relative high residence times between 3.5 and 6.0 days together with low ozone concentrations (< 47 ppb). Similar days with low ozone concentration are also found in July, August and, to a less extent, in June. The correlations are however better in those months than in May.

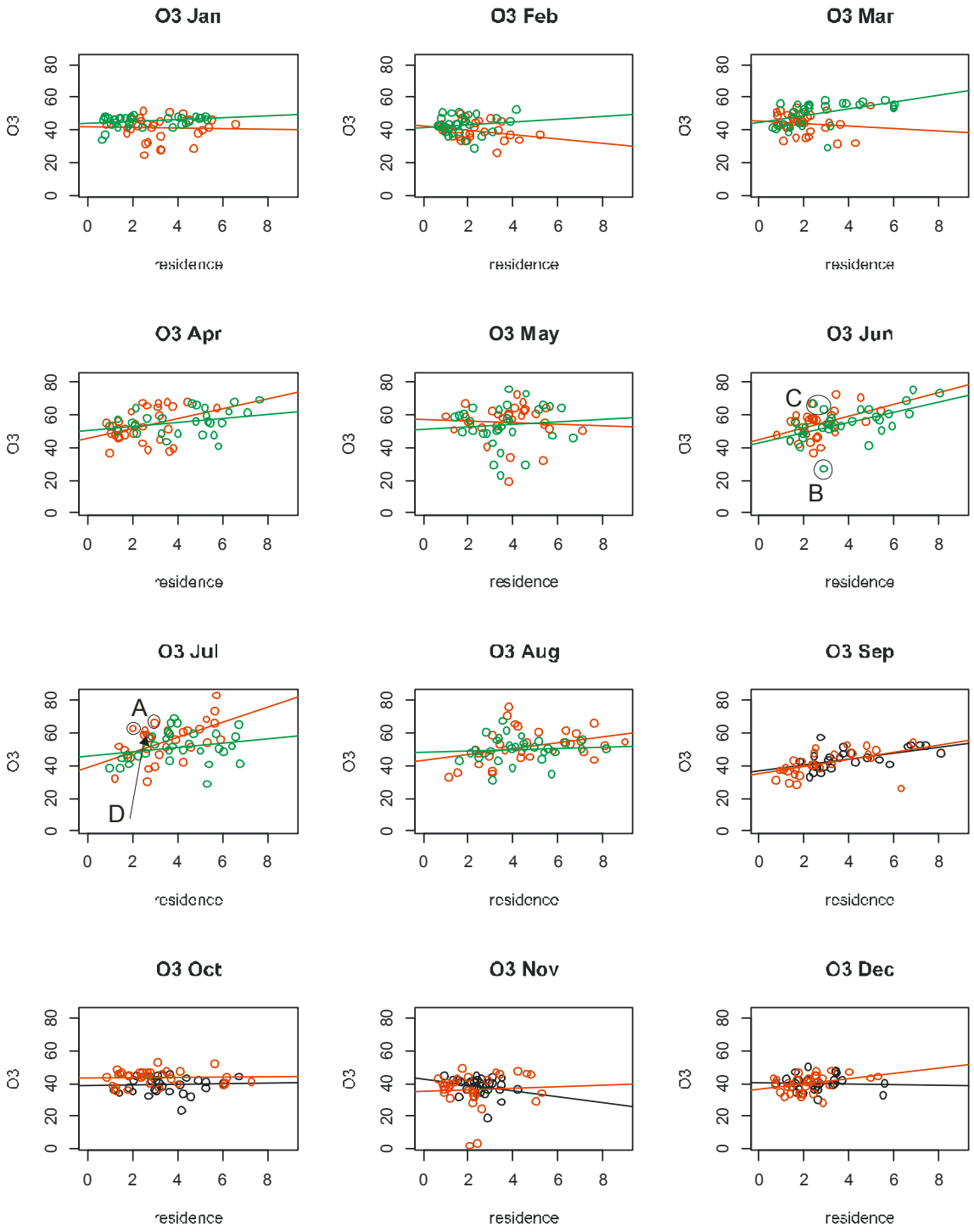


Figure 72: Relationship between ozone in Arosa and air parcel residence time over Europe calculated by trajectories ending at 06 UTC in Arosa. Empty circles refer to data points collected in different years. Black: 2000, red: 2001, green: 2002. Cases A, B, C and D are described later in text.

The results presented above contradict to some extent the results presented in the study of Pochanart *et al.* (2001) for Arosa ozone measurements (dataset 1996 – 1997). In that work the authors stated that, especially in spring and summer, the ozone concentration in Arosa increases noticeably whenever the air masses reside longer over the polluted European continent. This result was supported by correlation

coefficients R^2 (calculated from linear regression) above 0.6 and sometimes very close to 1.0 (except for the winter months December and January).

	2000		2001		2002	
	p	R^2	p	R^2	p	R^2
Jan	-	-	0.86	< 0.1	0.12	<0.1
Feb	-	-	0.15	< 0.1	0.52	<0.1
Mar	-	-	0.47	< 0.1	< 0.1	0.22
Apr	-	-	<0.1	0.13	0.12	0.10
May	-	-	0.75	< 0.1	0.66	<0.1
Jun	-	-	< 0.1	0.18	< 0.1	0.34
Jul	-	-	< 0.1	0.29	0.20	<0.1
Aug	-	-	< 0.1	0.13	0.70	<0.1
Sep	< 0.1	0.35	< 0.1	0.26	-	-
Oct	0.79	< 0.1	0.59	< 0.1	-	-
Nov	0.20	< 0.1	0.73	< 0.1	-	-
Dec	0.83	<0.1	<0.1	0.13	-	-

Table 30: Coefficients of linear regression calculated for the curves presented in Figure 72. Gray area: statistically significant slope (p-value < 0.1, obtained from t-test with confidence interval 0.01). Light gray: p-value between 0.1 and 0.15.

The discrepancies between the present study and the work of Pochanart *et al.* (2001) can be explained by the application of different methods. Firstly a different type of trajectories was used: Pochanart *et al.* (2001) used isentropic backward trajectories (based on ECMWF wind fields) as opposed to the trajectories used in this work (section 3.4). Possible influences on the residence time calculation could be analyzed by calculating both types of trajectories for the same site and for the same time period. This comparison was not attempted in this work. Furthermore Pochanart *et al.* (2001) used averaged ozone concentration over 12 hours whereas only morning data were considered here. The third difference lies in the statistical data treatment. Indeed air parcels in Pochanart *et al.* (2001) were categorized in different residence time classes as follows: air parcels were assigned as 1 day residence time if they had stayed over central Europe for a minimum of 0.5 up to 1.5 days; 1.5 to 2.5 days was assigned as 2 days residence time and so on. The linear regression was then calculated between the averaged ozone values for each residence time class. In order to perform a comparison between the present study and the study of Pochanart *et al.* (2001) air parcels were categorized in different residence time classes. Linear regression coefficients were recalculated. However, in order to grant less importance to less frequent events, classes containing only one day were excluded from the calculation and additionally the fit was weighted by the number of observations within each residence time class (Figure 73). Linear regression coefficients in Figure 29 indicate that this air mass categorization substantially improves the correlation between ozone in Arosa and residence time in most of the months. Positive correlations from March to September (except for May) are found with the highest values of the slopes found in June and July (about to 2.5 ppb O_3/ day over Europe). The results in Figure 73 better agree with the results of Pochanart *et al.* (2001). The categorization shown in Figure 73 is however supposed to be more reliable as the number of data points in each residence time class is considered in the weightening.

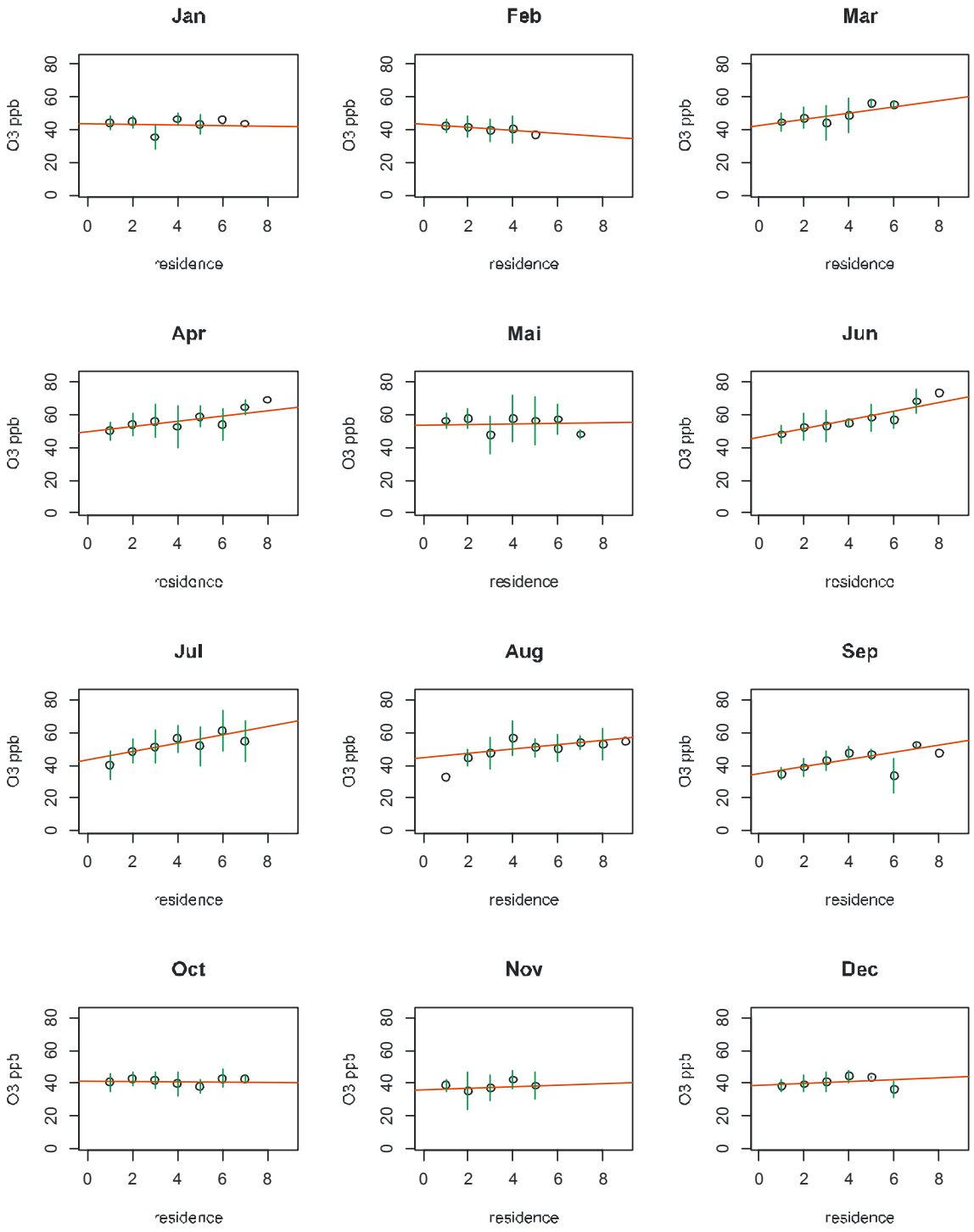


Figure 73: Relationship between ozone in Arosa and residence time of air parcel over Europe. Air parcels were categorized into residence time classes (see text). Fits were calculated with a linear regression. Correlation calculation considered the number of cases within each residence time class. Open circles: data with only one day in a class were not considered in the calculation. Bars: standard deviation relative to each class. The data were averaged over the two measurements years.

Month	p	R^2	Slope	*Month*	p	R^2	Slope
Jan	0.90	0.01	-0.13	Jul	0.04	0.62	2.52
Feb	0.05	0.79	-0.89	Aug	0.14	0.27	1.33
Mar	0.04	0.69	1.91	Sep	0.03	0.57	2.19
Apr	0.03	0.56	1.56	Oct	0.83	0.01	-0.09
May	0.89	0.01	0.20	Nov	0.69	0.06	0.43
Jun	< 0.01	0.86	2.65	Dec	0.39	0.19	0.60

Table 31: Correlation coefficients of linear regression calculated for averaged ozone within each residence time class. Gray area: statistically significant slope with p – value < 0.1, light gray: p-value between 0.1 and 0.15. (p-value calculated from t-test with confidence interval 0.01).

7.2 Factors causing deviation from the correlation

The difference between Figure 73 and Figure 72 has been explained to a large extent by the different data treatment. From the point of view of the different processes occurring in the atmosphere the effect of the categorization in different residence time classes is high and it obscures the ozone variability without explaining the origin of this variability. This variability is supposed to mainly depend on weather conditions experienced by the air parcel along its way to Arosa. On July and August 2002 the weather conditions (in Arosa) were generally worse than those in the corresponding months in 2001 which qualitatively could explain why no significant relationships were reproduced during these months in 2002 (Figure 72). In addition to weather conditions (a) other reasons leading to deviation from the correlation are: a different exposure to European emission (b), a different background concentration (c) and possibly relevant ozone contribution from high altitude (d).

The ozone background at “the edge of Europe” might change with respect to time and latitude. In a climatological study Wotawa *et al.* (2000) suggested an ozone background in the Atlantic region in the lower troposphere of 44 – 50 ppb (below 2500 m) changing according to the latitude along a north-south gradient. The lowest background concentrations were observed for the South Atlantic Ocean. This background concentration might be influenced by emission source regions located outside of Europe (e.g. North America or Asia). For example Li *et al.* (2002) estimated by a 3 D model including chemistry and transport that pollutants emitted on the North American continent contributes on average 5 ppb to ozone concentration at lower altitutude on the western part of Europe. This influence is not constant but varies with time (Stohl *et al.*, 2002).

The residence time over Europe does not account for all the factors mentioned above (a, b, c and d). For example, the background at “the edge of Europe” is considered as a constant quantity and the European continent is assumed to be a homogenously polluted region. The following discussion of selected short cases in June and July (labeled as A, B, C and D in Figure 72) illustrates the influences of these factors. On the 6th and 7th of July 2001 (case A) trajectories and meteorological measurements indicate south advection from the polluted Po basin and an enhanced ozone concentration (63-66 ppb) was measured in Arosa. The positive deviation from the fit calculated between residence time and ozone (Figure 72) could be explained by the fact that the low residence times (2-3 days) did not account for the high emissions in the Po basin. On the 25th of June 2002 (case B) ozone concentration in Arosa (~27 ppb) was strongly influenced by a front passage (as described in section 5.4.2). The negative deviation from the fit between residence time and ozone can be attributed to

the fact that the residence time did not account for the weather conditions which, in this case, favored advection of fresh and ozone-poor air from the boundary layer. In the same range of residence time on the 1st and 2nd of June 2002 (case C) a clearly higher ozone concentration (63 and 66 ppb) was measured. The positive deviation from the fit between residence time and ozone could have been influenced both by enhanced photochemical ozone production due to the fair weather conditions during those days and by a higher ozone background as suggested by the trajectories originating over the North American continent. Finally on the 22nd of July 2001 (case D) short after midnight a sharp ozone increase from about 46 ppb (at 00 CET) to about 60 ppb (at 05 - 06 CET) took place. During this time CO concentration slightly decreased from 140 to 132 ppb, NO_y concentration was unusually low (<1 ppb) and relative local humidity dropped from 60% to less than 20%. Trajectories arriving at 06 UTC were all coming from high altitude; 4 out of the 5 trajectories originated from an altitude of < 400 hPa. Despite the relative low deviation from the fit between residence time and ozone, it appears obvious that ozone on that morning (58 ppb, between 03-06 CET) was not directly determined by European emissions (2.6 days over Europe) but was mainly caused by an intrusion of ozone rich air from high altitude possibly with a contribution by stratospheric ozone.

Among the above listed uncertainties (a,b,c,and d), weather conditions experienced by air parcels and information about pollution degree within regions crossed by air parcels are supposed to be the most relevant quantities ignored in the residence time analysis as presented in Pochanart *et al.* (2001). Other pronounced events like the one on the 22nd of July 2001 (case D in Figure 72) were not detected in the warm season.

An additional event showing the importance of weather situation for ozone in Arosa is the time series between the 8th and the 11th of August 2002 (Figure 74). Weather conditions rapidly deteriorated after the 8th as a consequence of cyclonic weather over a large part of the continent. The ozone concentration in Arosa steadily decreased within 3 days from about 70 ppb to much lower values (< 30 ppb) although residence time tended to increase. This event shows that increasing residence times of air parcels over Europe does not necessary lead to high ozone concentration in Arosa at least when bad weather conditions prevailed over Europe.

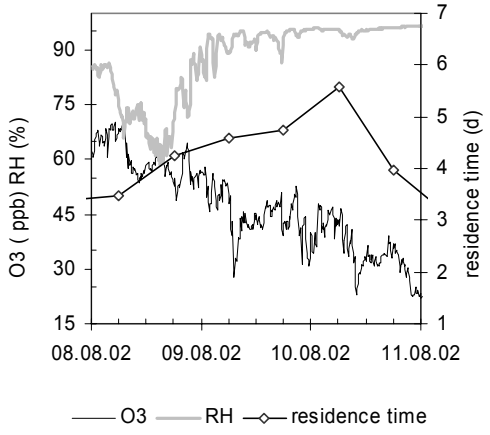


Figure 74: Time series of ozone (O_3), relative humidity (RH) and air parcel residence time in Arosa at the beginning of August 2002.

7.3 Weather conditions and residence time analysis

In the following sections weather conditions are analyzed with different methods and with focus on the photochemically more active warm season. Indeed weather conditions play an important role in tropospheric ozone production. In particular radical formation is dependent on availability of (UV-) solar radiation (section 2.1). If ozone concentration in Arosa is correlated with residence time over Europe, this correlation should be more pronounced for air parcels which experienced the fairest weather conditions along their path toward Arosa.

7.3.1 Synoptic weather and fronts

In chapter 3.3 the synoptic weather classification according to Schüepp was introduced. By analysis of different meteorological parameters it is possible to define the daily synoptic weather type for a region including the Swiss Alps and the Swiss plateau. The corresponding weather type was assigned to each day in the dataset. In other words the classification applied describes the synoptic weather during the last day along the trajectory ending in Arosa. Figure 75 shows the relationship between ozone and air parcel residence time for different weather classes during the months April, June, July and September. Compared to April and September, June and July data show prevalence in the convective weather types “anticyclonic” and “indifferent” whereas advective weather conditions clearly occurred less frequently.

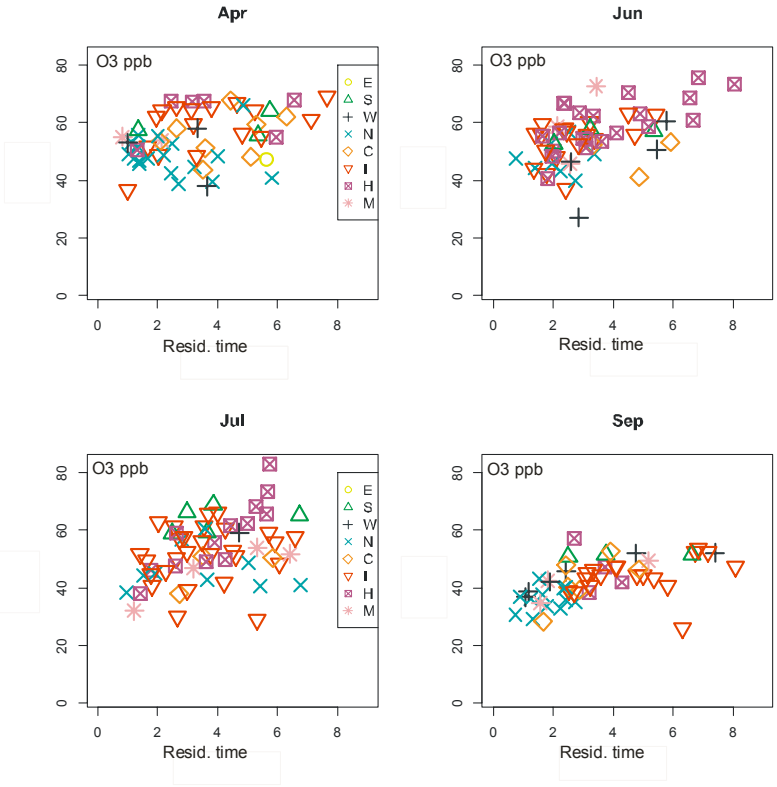


Figure 75: Relationship between ozone concentration (O_3) in Arosa and residence time for the months April June, July and September. Information on the different weather types is included. E east -, S south -, W -, N – advection, C – cyclonic, I indifferent, H anticyclonic, M mixed.

A clear positive correlation between ozone and residence time in the 2 summer months June and July is achieved for days in which anticyclonic conditions prevailed (June: R^2 0.44, slope 3.2 ppb / day over Europe, intercept 47.7 ppb; July: R^2 0.76, slope 7.1 ppb / day over Europe, intercept 30.0 ppb).

This result could be explained by the most favourable conditions for photochemical ozone production occurring during such a weather type. These are cloudless sky due to general subsidence, high solar radiation and generally high temperature. A closer analysis of these June and July days revealed that only in 4 times out of 32 single days with anticyclonic weather occurred. In the remaining cases they occurred as longer episodes. This observation is plausible with the stability and the large scale extension of this weather type. Days with anticyclonic weather conditions and low ozone concentration were found after a period with bad weather, typically after a front passage. Within the longer episodes with anticyclonic weather, ozone concentrations generally increased day after day along with an increasing residence time. The latter observation suggests that the positive tendency in June and July between residence time and ozone described in section 7.1 was partly determined by these single episodes. Section 7.3.3 describes two of these episodes in more details. In August 2002 (between the 14th and the 20th) a fair weather episode (by "indifferent" weather) with ozone increasing day after day in Arosa (from about 45 ppb to 55 ppb) was found as well. Again ozone increased together with increasing value of residence time. Despite high correlation (R^2 = 0.8, 2 ppb/ day over Europe) the slope of this prolonged event was not "strong" enough to determine a clear correlation for the entire month.

Only few days with anticyclonic conditions occurred on September. In this month the positive and significant correlation (section 7.1) is the result of different synoptic weather types and is partly driven by the northerly advection cases which, in September, were all associated with low values in residence time. These values were often associated with a front passage (Figure 76) and were thus most probably connected with transport of ozone-poor air from the boundary layer (see also Figure 57). This implies that the positive slope between ozone and residence time is not only to be interpret as the result of photochemical activity, but is also influenced by ozone loss processes. This observation suggests that attempts to estimate the ozone hemispheric background by using the correlation between residence time and ozone in Arosa might lead to underestimated values. For example Pochanart *et al.* (2001) calculated a hemispheric ozone background for September of 30 ppb by extrapolating the correlation to 0 days residence time, which would well agree with Figure 75. Zellweger *et al.* (2002) suggested instead for Jungfraujoch an autumn averaged ozone value of 49 ppb for undisturbed free troposphere conditions. These two contrasting results emphasize the problem of the estimation of background ozone by using the residence time analysis.

Figure 76 indicates that generally also in other months such as April, June and July many days showing low ozone concentrations were influenced by a front passage. During these days the measurements were most probably influenced by ozone titration processes occurring in the boundary layer.

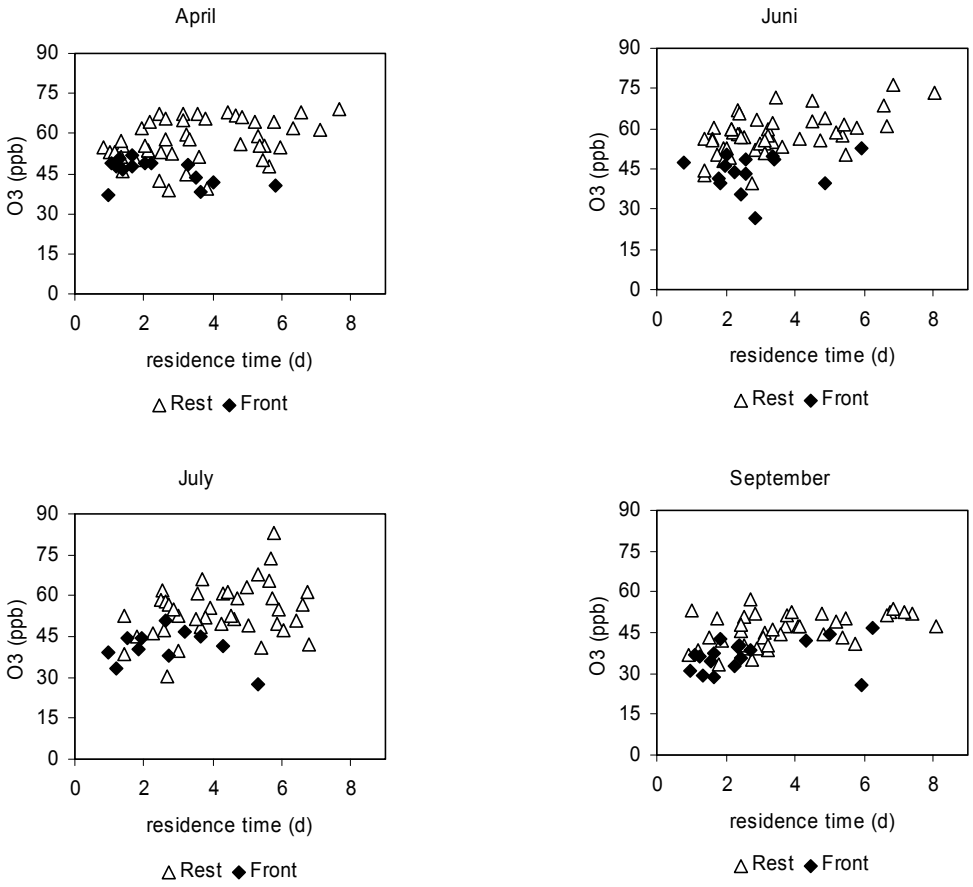


Figure 76: Same picture as in Figure 75 whereby days influenced by a front passage are separated from the entire data set. Front passage was determined according to the Alpine Weather Statistics inventory (parameters 18 and 21) and relative humidity in Arosa (>80%).

The advection weather type “South” and “North” did not show any dependence of ozone on residence time. This pattern can be observed for every single month (Figure 75). The behavior for southerly advection days could be explained by the considerable amount of pollutants emitted in the Po basin leading to enhanced ozone formation in summer (see also section 5.3). The result suggests that for southerly advection a longer history of an air parcel is a less important factor compared to the influence of the strongly polluted Po basin (see next section 7.3.2). On the other hand northern advective weather is often connected with humid and rainy weather which, as said above, is not favorable for ozone formation.

7.3.2 Foehn cases

In section 5.3.3 south foehn events were selected according to different meteorological parameters. Trajectories for these cases clearly showed that air parcels crossed the Po basin (Figure 44). For these events the relation between ozone and air parcel residence time over Europe was analyzed (Figure 77).

Limited to only south foehn events the ozone concentration in Arosa is independent of residence time of air parcel over Europe. According to trajectories air parcels usually travel fast over the Po basin (section 5.3.3), however they often travel before over Spain, France or even Central Europe before moving over the Po basin. This

explains why foehn events have sometimes relatively high residence time (see section 5.3.2 where a foehn event is described as having low residence times over the Po basin and compare those values to the much higher residence time over Europe between 3.7 and 4.4 days). Ozone concentration in Arosa does not increase with every additional day residence time.

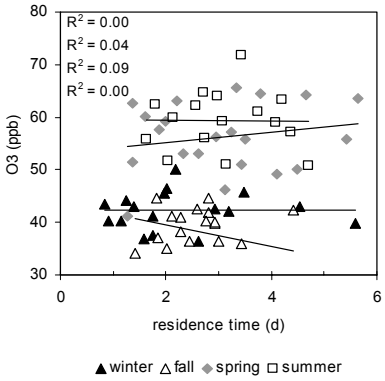


Figure 77: Relation between ozone in Arosa and air parcel residence time over Europe for south foehn cases selected according to criteria described in section 5.3.3. Correlation coefficients R^2 from linear regression refer to (from top to bottom): summer, spring, fall, winter.

Similarly to synoptical southerly advection this result can be explained by an enhanced importance of a passage over the strongly polluted Po basin rather than by a longer history of an air parcel. Significant differences are found among the seasons with generally high ozone concentrations in spring and summer and low concentrations in winter and fall as already discussed in section 5.3.3.

7.3.3 Summer events with strong correlation between ozone and residence time

Figure 78 shows strong positive correlations between ozone in Arosa and air parcels residence times for 2 summer periods. Both periods were characterized by fair weather conditions throughout large parts of Europe due to the influence of high pressure systems. At the same time ozone time series indicated a general increasing tendency in concentration (see also time series in section 5.4.1). During the first period (end of July 2001) ozone concentration in Arosa increased after the passage of a weak perturbance (registered at the end of the 23rd) from about 40 ppb on the 24th to over 80 ppb on the 30th, decreased on the 31st and increased again on the 1st of August (Table 32). According to the trajectories reported in Figure 79 the distinct flow patterns on these days were very similar among each other, mainly representing air parcels moving from the Atlantic to south Scandinavia and later towards the Alps.

Similarly, in the second period in June 2002 ozone in Arosa increased from about 40 ppb on the 13th to 75 ppb on the 19th. Afterwards its concentration varied between 80 and 60 ppb (Table 32). Also this period occurred immediately after a bad weather period characterized by a front passage. Trajectories showed in this case that air parcels were mainly advected from a W – SW sector (Figure 79). On the first part of this June period air transport to Arosa occurred extremely fast and originated from the Atlantic Ocean. Starting from the 15th, air parcels stayed substantially longer over Europe (over Spain and South of France) and, beginning from the 20th, trajectories indicate that before arriving to Arosa air parcels had passed over the Po basin.

The changes in residence times (Table 32) and the 2 strong positive correlations suggest that, within each case, the issue about origin of air parcels was less relevant in determining ozone in Arosa relative to the issue about how long air masses stayed over the polluted continent. Beginning from a low value ozone concentration increased, on average, with increasing residence times. This suggests that a low ozone concentration (background) is superimposed by a term "transport of well aged air" which is dependent on emissions occurring along the trajectories and on weather conditions. This term seems to be described by the residence time over Europe. In the July case the increase amounted to 14.5 ppb/day over Europe while in the June case the increase was lower about 4.1 ppb O_3/ day over Europe.

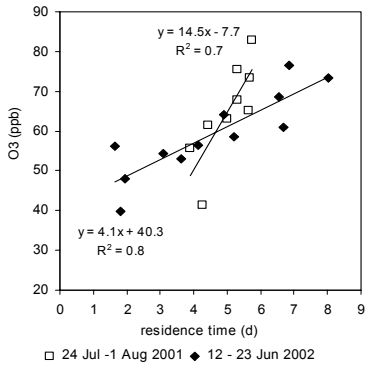


Figure 78: Correlation between ozone in Arosa and air parcel residence time for two periods characterized by fair weather.

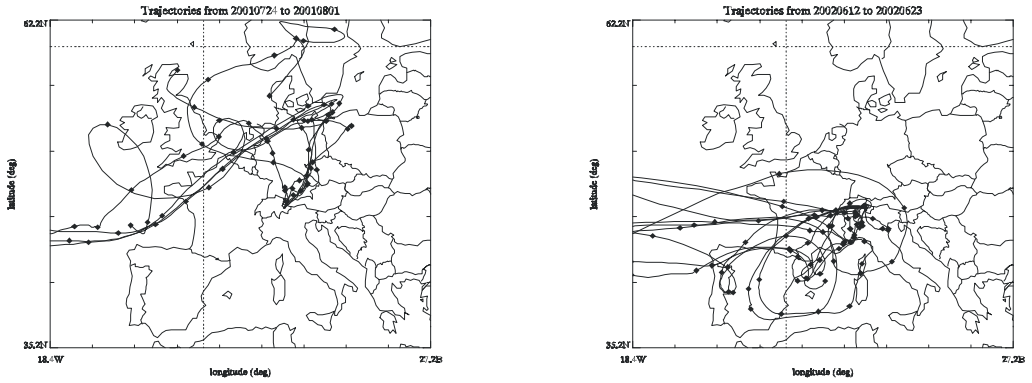


Figure 79: Trajectories for the periods from the 24th July to 1st of August 2001 (left) and from the 13th to the 21st of June 2002 (right). Marks define 24 hours intervals.

The correlation of the June case (Figure 78) could be also interpreted in a different way according to information contained in Table 32 and to the flow pattern of trajectories described above (Figure 79). Indeed the strong ozone increase (about 15 ppb) occurring from the 12th to the 14th was rather independent of the air parcel residence time over Europe (Table 32). Similarly the NO_y concentrations did not provide evidence that air parcels were traveling over higher polluted area during these days. The reason of such increase can be rather found in the switch of weather from bad to fair conditions. The increasing value of surface solar radiation along the trajectories (SSR in Table 32, see also section 3.4.4) suggests that for this first ozone increase time after the front passage (with insulation) rather than residence time over Europe was important.

From the 14th to the 15th June a rather large increase in residence time took place although no change in ozone was found. On the three days following this date ozone concentration slightly increased along with an increase in residence time. Both ozone and residence time strongly increased on the 19th. From these days on both quantities remained at a high level until the end of the period. The NO_y concentrations, used here as a measure of emissions (section 2.1), suggests that air parcels had also crossed a strongly polluted area. Indeed trajectories ongoing from the 20th distinctly show an air parcel passage over the Po basin before arriving in Arosa.

Time	Ozone (ppb)	Res. Time (d)	NOy (ppb)	SSR (10e+6 J/m2)
June case				
12.06.02	39.9	1.83	2.16	5.3
13.06.02	48.1	1.95	1.79	7.6
14.06.02	56.2	1.63	2.11	9.3
15.06.02	53.1	3.64	1.40	10.5
16.06.02	54.3	3.10	1.72	11.5
17.06.02	56.4	4.13	2.20	11.1
18.06.02	58.6	5.19	2.59	10.9
19.06.02	76.5	6.84	5.81	11.0
20.06.02	73.4	8.04	4.45	10.2
21.06.02	68.6	6.56	7.70	10.5
22.06.02	64.1	4.89	3.47	10.4
23.06.02	61.0	6.68	8.85	10.4
July case				
24.07.01	41.5	4.27	1.07	9.3
25.07.01	61.5	4.44	3.74	9.0
26.07.01	55.5	3.91	3.26	8.7
27.07.01	65.3	5.65	3.77	8.8
28.07.01	67.9	5.29	3.50	8.7
29.07.01	73.4	5.66	5.22	9.6
30.07.01	82.8	5.75	6.61	9.3
31.07.01	63.1	4.99	3.60	9.3
01.08.01	75.4	5.32	5.83	9.2

Table 32: Ozone and NO_y concentration in Arosa (averaged between 03 and 06 CET), air parcel residence time over Europe. Mean surface solar radiation (SSR) from ECMWF fields along trajectories.

In section 5.3 it was found that the Po basin causes high ozone concentrations in Arosa during summer. In section 7.3.2 it was shown that, for south foehn events in summer, the ozone concentration in Arosa is independent of air parcels residence time. The strong correlation between ozone and residence time (Figure 78) was driven by low ozone values at the beginning and by the high ozone values at the end of the considered June period. This alternatively suggests that the strong correlation found within the June case could also just be explained by the influence of the weather and of the origin of the air parcels. Low ozone values at the beginning of the period were still influenced by previously occurring bad weather and high ozone value at the end could have been mainly determined by the passage of air parcels over the Po basin.

The July case also shows a very strong ozone increase during the beginning of the considered period (20 ppb within a single day, see Table 32). The SSR values on the

24th do not present lower values indicating the passage of the perturbation over Europe. Most likely this perturbation was too weak to be resolved by the ECMWF-data. Compared to the June case this stronger ozone increase could be explained by the fact that air parcels arriving in Arosa had been in contact with a larger amount of fresh emission as NO_y concentration suggests. As soon as the weather conditions were fair ozone concentration rapidly increased. The flow pattern on these days was very similar (Figure 79) and emissions were most probably more homogeneously distributed along the air parcel paths (in contrast to the June case were the highest polluted area (Po basin) was crossed by the air parcel only towards the end of their travel to Arosa). This might qualitatively explain why higher ozone concentrations were reached in a relatively narrow residence time spectrum. This July event is more in accordance with the first interpretation given above with residence time being a good estimate for pollutant uptake by the air parcels. However the very low ozone concentration on the 24th was still influenced by the perturbance. Considering only the period from the 25th on, the correlation (R^2=0.7) has a slope of 11 ppb/day over Europe. Wotawa *et al.* (2000) analyzed the temporal development of the simulated ozone concentration (with the IMPO Lagrangian photochemical box model) along the trajectories approaching the alpine region and found for the summer half – year maximal increase in ozone in the air parcel amounting to 6-13 ppb in the last 24 hours of transport that can be qualitatively compared with the value found in this particular case.

For both cases it was again found that correlations were also determined by low ozone values which were found after a bad weather period. Thereafter one could conclude that it is more convenient to compare days with similar weather conditions along the trajectories. In particular this is important with respect to statements about ozone production rate over Europe. The alternative interpretation given for the June case suggests that residence time does not account for the spatial distribution of emission within the European continent which could be important in some cases.

7.3.4 Ozone, residence time and relative humidity in Arosa

Two methods were applied to check for the correlation between residence time and ozone for days with comparable weather conditions. The first method described here is based on relative humidity and the second (next section) is based on surface solar radiation (SSR) field from ECMWF.

Section 6 discussed the diurnal variation in air pollutants based on subdivision into classes with different relative humidity. May to August days were similarly separated into 4 classes (RH 1 to RH 4) according to the 25%-, 50%- and 75%- percentile of relative humidity. Class RH 1 groups days with the lowest value in relative humidity, while RH 4 includes all days with the highest values. Figure 80 shows that practically all days with the lowest ozone concentration also corresponded to the moistest days (RH 4).

Obviously these days were characterized by bad weather conditions. Independent of air parcels residence time ozone observed in Arosa on these particular days is the result of a diminished photochemical activity due to covered sky over the European continent and loss processes occurring in air parcels arriving in Arosa. No correlation was achieved between ozone and residence time during these days. This result also generally shows the limit of ozone as a tracer. Ozone can be subjected to titration and dry deposition and thus does not fulfill all the basic requirements of a perfect (chemical) tracer (Stohl, 1998). Correlations became substantially larger in the

relative humidity class RH I. This was most pronounced in May, June and July which show significant slopes increasing from May (2.35 ppd/day over Europe) to July (3.23 ppb/day over Europe). Assuming that relative humidity measured in Arosa includes, to some extent, information about the weather experienced by the air parcel before arriving at the measurement site, this class I represent days with the most favorable conditions for ozone production. In August the analysis did not show any remarkable trend. In this month ozone concentrations were higher during days with low values of relative humidity. However no correlation with residence time was found.

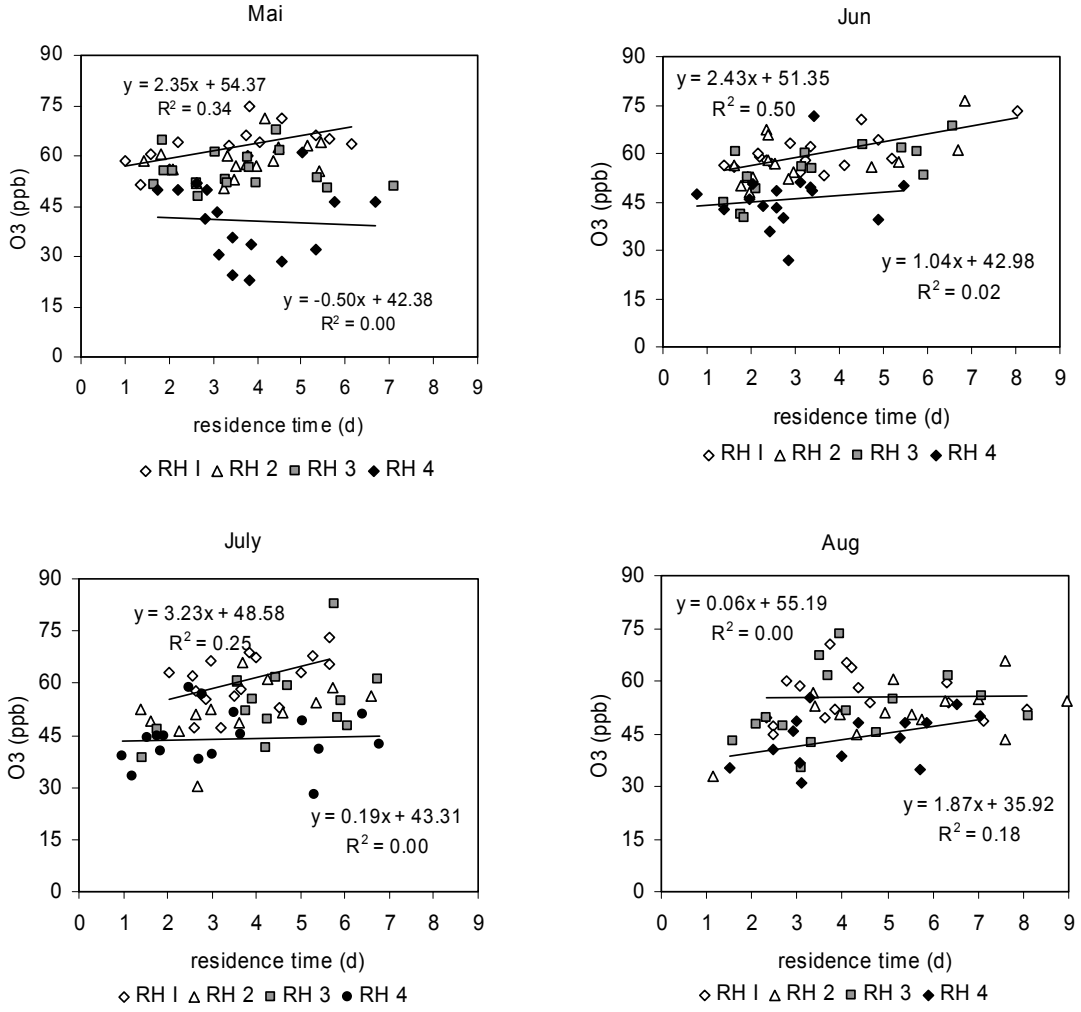


Figure 80: Correlation between residence times of air parcels over Europe and ozone concentration in Arosa for May, June, July, August. Ozone concentrations are grouped according to 25%- , 50%- , and 75%- percentile of relative humidity in Arosa (measured between 03 and 06 CET). Linear regressions are only depicted for class RH 1 and class RH 4.

The similar approach was also applied using local temperature. However no better results were achieved than those represented in Figure 80. Such an approach has the main advantage to be simple and fast to implement. However an issue arises about the representativity of local meteorology for air parcels history. With the following method the weather situation over larger region is considered. This improved the validity of data separation as, potentially, the weather situation along the trajectory is better described.

7.3.5 Ozone, residence time and surface solar radiation

The total surface solar radiation (SSR) from 2 dimensional fields of ECMWF available for 00 and 12 UTC was assessed along the trajectories of June and July 2001 and 2002 (section 3.4.4). SSR is not just equal to the range of radiation relevant for ozone production. The relation between both global radiation and UV radiation is rather complex, e.g. thin or scattered clouds can, for a short time, increase UV above what it would be on a blue sky day by further scattering the radiation (Bremaud & Taupin, 1998). In addition the proportion of UV to global radiation has been suggested by many authors to be generally smaller for clear sky conditions than for cloudy conditions (Ambach *et al.*, 1991). On the other hand it was shown that clouds reduce the UV-radiation, in an annual mean sense to levels from 62-78% of the values that would exist if the sky remain clear (Frederick & Snell, 1990). For these reasons SSR can only represent a qualitative indicator for the actual relevant UV-radiation. Figure 82 depicts the information contained in these solar radiation fields for 2 events (22nd of June 2002 and 15th of July 2002). Air parcels arriving early morning in Arosa on these 2 days came from different direction. However they show a similar value in residence time (Table 33). Quite similar values for CO and NO_y concentrations were found suggesting that, on average, both trajectories travelled over a similarly polluted area. Despite these similarities ozone concentrations observed on the 2 early morning times in Table 33 differ on average by 23 ppb. This large difference in ozone was mainly caused by the generally bad weather conditions prevailing during the July case over central Europe. A comparison of relative humidity values provides evidence for the different weather conditions in Arosa (Table 33).

	Residence time (days)	Ozone (ppb)	RH (%)	CO (ppb)	NO_y (ppb)
22.06.2002	4.9	64.0	59	133	3.47
15.07.2002	5.4	41.0	94	140	2.70

Table 33: Air parcel residence time over Europe, ozone, CO, NO_y and relative humidity in Arosa (average between 03 and 06 CET).

Satellite images for the 22nd of June 2002 show a completely cloudless sky over Europe. On the previous days sky over northern Europe was covered due to perturbances crossing the continent at high latitudes.

According to trajectories air parcels arriving in Arosa on the 22nd (early morning) were not affected by clouds as they came from the south (Figure 82).

The regime of SSR along the trajectory in Figure 82 shows clearly values higher than those for the second event (15th of July). This result is most pronounced during the last 50 – 60 hours of the trajectory path. Indeed satellite images show for the second event (15th, 14th and on the 13th) an almost completely covered sky over Northern Italy, Switzerland and Southern Germany whereas less coverage was observed on the 10th, 11th and 12th. The minimum in SSR for the event of the 15th, occurring about 25 to 55 hours before the trajectory arrival in Arosa, can also be compared with the cold front passage registered in Zurich between 00 and 12 UTC of the 13th.

In this case the SSR along the trajectories qualitatively agrees with information on sky coverage learnt from weather chart and satellite images. SSR also qualitatively explain the difference found in ozone on the two events by the different radiation condition encountered by the air parcels moving towards Arosa.

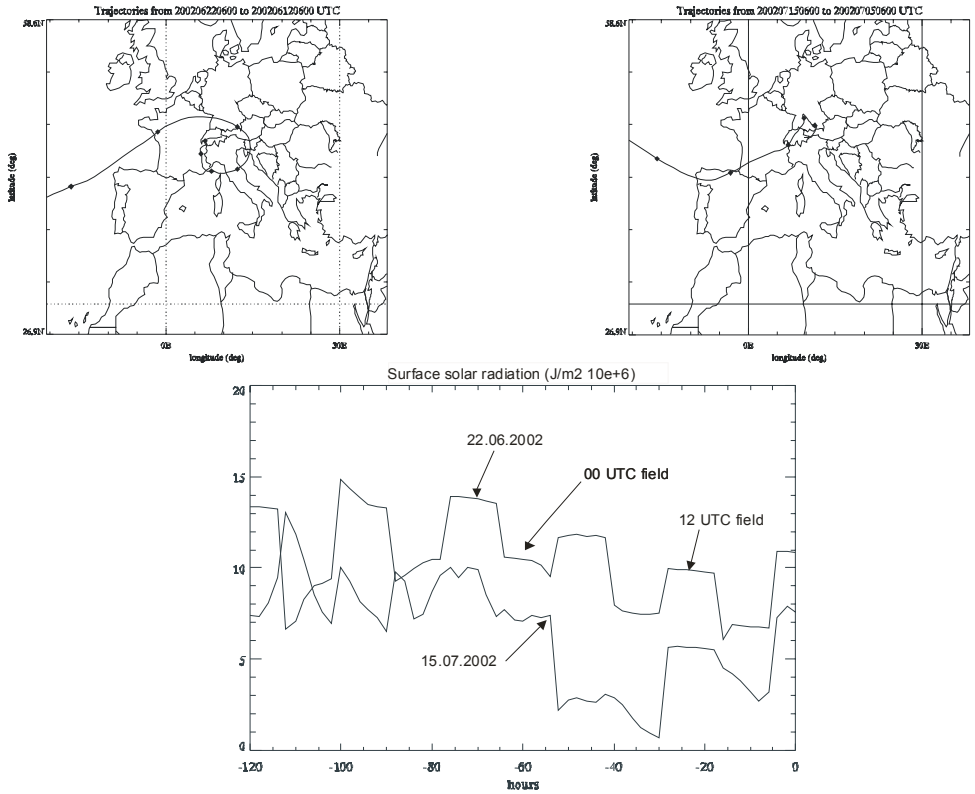


Figure 81: Trajectories ending in Arosa at 06 CET and surface solar radiation (SSR) along the trajectories on the 22nd of June and 15th of July 2002. Marks define 24 hours intervals. The abrupt changes in SSR are caused by different ECMWF fields that are accounted along a trajectory in a consecutive way. Due to temporal resolution of the 2 fields at 00 UTC and 12 UTC the latter shows the highest mean values because the 2 sunniest hours of the day (11-12 and 12-13 CET) are accounted into this field.

June and July ozone measurements in Arosa were analyzed through SSR. Days were classified into 4 classes (SSR I, SSR II, SSR III and SSR IV) according to the 25%- , 50%- and 75%- percentiles of the mean values of SSR. From the analysis monotonically decreasing ozone concentrations were found starting from days with highest radiation along the trajectories (SSR IV) to days showing the highest degree of sky coverage (SSR I) (on average 61.1 ppb in SSR IV, 56 ppb in SSR III , 49.6 ppb in SSR II and 47.7 ppb in SSR I). The correlation between ozone in Arosa and air parcels residence time were found to be significant for the most sunny days along the trajectories (SSR IV: R^2 0.41, slope 2.5 ppb/day over Europe; SSR III: R^2 0.30, slope 4.1 ppb/day over Europe). No positive tendencies were instead found within class SSR II and class SSR I. This confirms what found through the application of the simple approach using relative humidity (section 7.3.4); namely ozone concentration does not depend on the residence time of air parcels over Europe when the weather is generally not fair.

Despite its coarse resolution and its definition as sum parameter SSR can be considered a good tool to discriminate among days with fair weather conditions in summer (in winter time the discrepancy between SSR and the amount of radiation actually “viewed” by the air parcel traveling at higher altitude than the surface could be larger than in summer due to the formation of stable inversion layer).

In classes SSR IV and SSR III highest ozone concentration were found along with typically high NO_y concentrations. This results in a positive correlation between O_3

and NO_y (Figure 82) which provides evidence for a rather recent photochemical origin of ozone. NO_y can thus act as a measure of NO_x emission during days with the most favorable conditions for photochemical activity (see section 2.1).

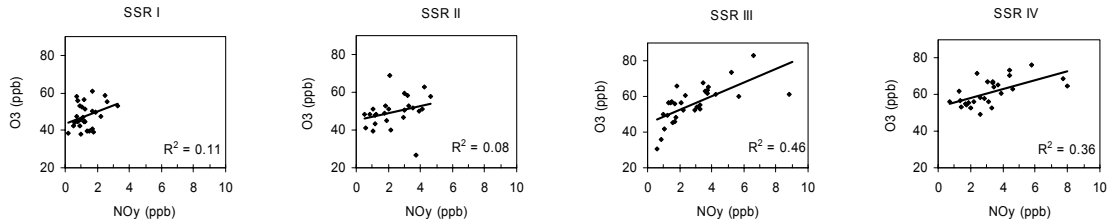


Figure 82: Correlation between ozone and NO_y concentrations in Arosa within SSR classes I to IV. SSR I include days with highest degree of sky coverage along trajectories. SSR IV include days with lowest degree of sky coverage.

Days falling in each SSR class were further grouped according to NO_y concentration measured at the arrival time of the trajectory. The distinct categories of NO_y concentrations will be referred to as: low NO_y (< 33%-percentile), middle NO_y (between 33%- and 66%-percentile) and high NO_y (> 66%-percentile)

The results of the analysis are summarized in Table 34 and depicted in Figure 83. The number of days considered in each class of this table is rather small; every fit is obtained with maximum 12 – 13 events which limit to some extent the robustness of these results. As said above however, the slope within SSR IV and SSR III were significant also without any categorization into NO_y classes.

	SSR I			SSR II		
	R^2	Slope	Intercept	R^2	Slope	Intercept
High NO_y	0.10	1.3	41.7	0.09	3.4	41.2
Mod. NO_y	0.27	1.8	43.7	0.20	2.1	43.7
Low NO_y	0.00	0.2	46.0	0.16	1.4	42.1
	SSR III			SSR IV		
	R^2	Slope	Intercept	R^2	Slope	Intercept
High NO_y	0.43	3.7	49.4	0.49	2.0	57.0
Mod. NO_y	0.17	2.3	48.4	0.33	3.1	50.1
Low NO_y	0.25	3.2	36.6	0.28	1.2	51.1

Table 34: Correlation coefficients of linear regressions calculated for each SSR-class: R^2, Slope (ppb O_3/day), Intercept (ppb O_3). Gray area represents correlation with significant slope ($p<0.1$, calculated from t-test with confidence interval 0.01). Light gray significant slope with confidence interval 0.05. Days within each SSR class were grouped according to NO_y concentration. Every slope is calculated from a data set containing about 12 – 13 events.

Slopes within SSR IV and SSR III are almost all significant and vary from 1.2 to 3.7 ppb O_3/day over Europe. The different slopes within a class can be interpreted as attempt to separate days in which air parcels passed over a polluted area from days in which air parcel crossed a less polluted area. Within SSR IV slopes are, for each NO_y category, lower than those for SSR III. This could be interpreted as the result of the slow down in ozone increase which is normally observed after the rapid ozone increase phase observed in summer smog episodes (Dommen *et al.*, 1995).

Since days showing bad weather along trajectories (and showing low ozone concentrations) were neither considered within class III nor in class IV the slopes found are not as large as those reported by Pochanart *et al*. (2001). These ranged between 3.8 and 6.6 ppb/ day over Europe in summer months.

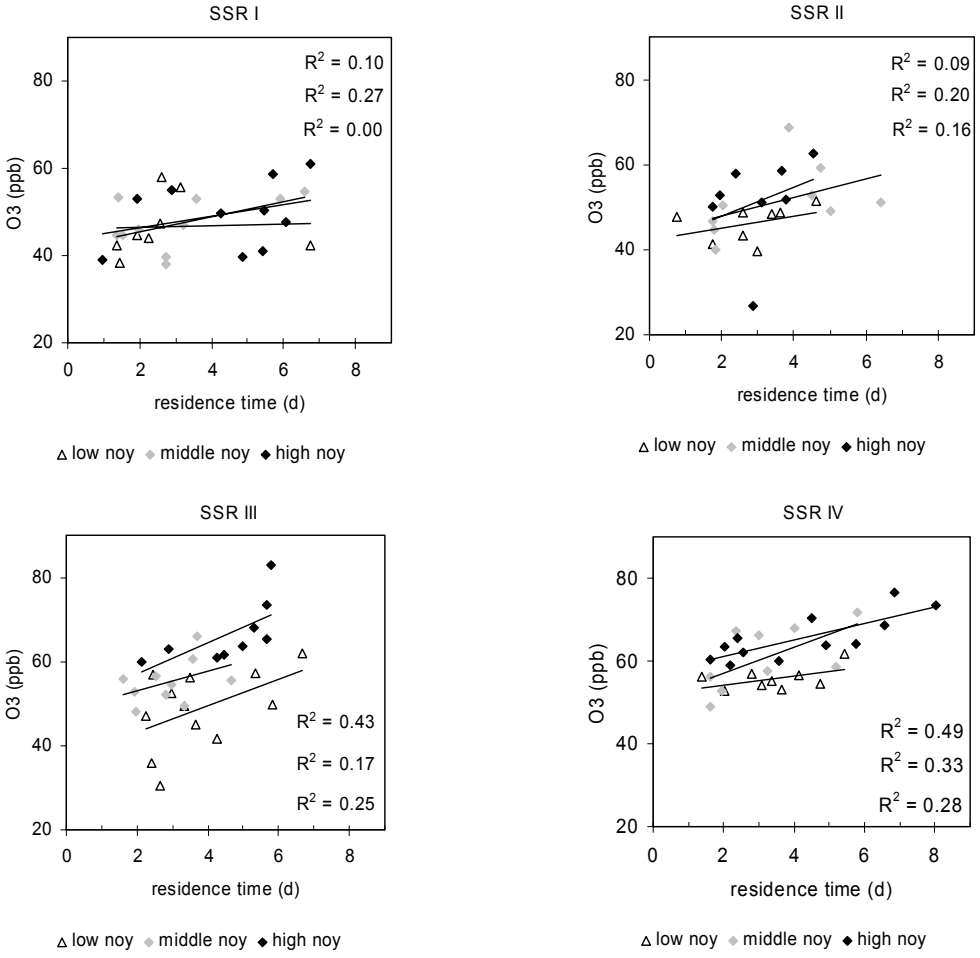


Figure 83: Relation between ozone and air parcel residence time over Europe for June and July data (2001 and 2002). R^2 (correlations coefficient) from top to bottom for high NO_y, middle NO_y and low NO_y.

In a recent study Naja *et al.* (2002) applied the residence time analysis to ozone sounding performed in Payerne and in Hohenspeissenberg. Results showed an ozone production rate of about 2 ppb/day over Europe in the lower troposphere (750 hPa to 550 hPa) in summer. Assuming that ozone in this layer is less influenced by weather changes than in the boundary layer the slopes for SSR IV and SSR III in Table 34 qualitatively agree more with Naja's findings. The slightly higher averaged slope values could be regarded as an enhanced exposition of air parcels arriving in Arosa to boundary layer emissions.

Figure 84 shows the frequency of the synoptical weather types (introduced in section 3.3) within the 4 SSR classes. Again it is found that within the fair weather classes IV and III the convective weather type occurs more frequently. However classes SSR I and SSR II also display 9 days with anticyclonic weather. These days are typically associated with low ozone concentration. This finding is indirectly confirming a

previously cited observation (section 7.3.1) about these days being typically found after a period characterized by bad weather.

The analysis presented in the current work is believed of more suitable application in the investigation of the relationship between ozone and residence time. This is because it offers the advantage of comparing days with similar weather conditions along trajectories (here represented by the amount of SSR). This parameter is a qualitative estimate of the amount of available (UV-) radiation along the trajectories. Slopes determined for class SSR IV and class SSR III are minimally influenced by bad weather. Low ozone concentrations possibly due to loss processes during such meteorological conditions do not appear in these classes. Within classes SSR IV and SSR III one could theoretically expect the different slopes to cross the O_3 - axis at the same point corresponding to a simple estimate of Atlantic background in summer (Table 34, intercept). With the exception of the slope found for SSR III relative to low NO_y (which seem to be influenced by 2 outliers) it is estimated an ozone background of 51 ± 3 ppb. This background level is slightly lower than the summer mean ozone concentration determined for the Jungfraujoch under free tropospheric influence (57 ± 10 ppb) (Zellweger *et al*., 2002). At the same time this value is clearly higher than the 32 ppb given by Derwent *et al.* (1998) for June-July as representative for the hemispheric background. This latter estimate is however strongly influenced by the maritime boundary layer as it was calculated from measurements performed at Mace Head (sea side) during advection from the Atlantic Ocean. Wotawa *et al.* (2000) instead proposed an ozone concentration of 44-50 ppb for typical background in the Atlantic Ocean region below 2500 m whereas Naja *et al.* (2002) estimated an hemispheric ozone background of 50-52 ppb in June – July in the lower troposphere (750 hPa to 550 hPa) by applying residence time analysis to ozone sounding. Finally the estimated background value of 51 ± 3 ppb is somewhat higher than the concentration of 40-50 ppb found as typical undisturbed from European emissions during the July 2001 event described in 5.4.1.2.

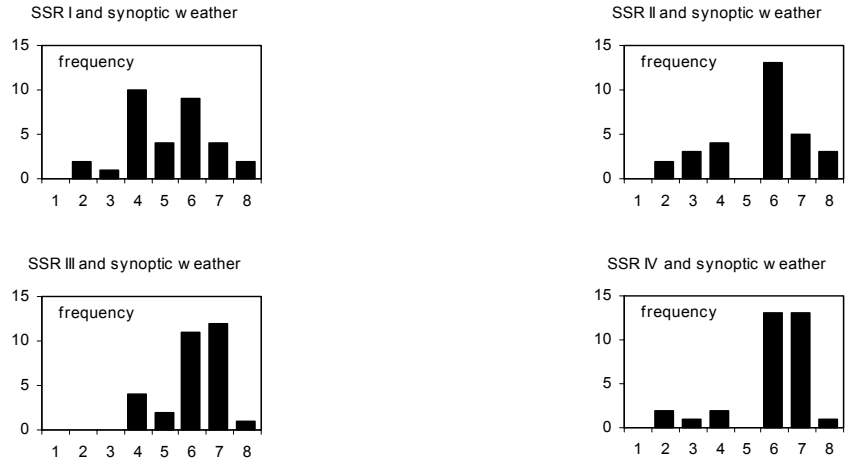


Figure 84: Frequency (# cases) of synoptical weather types within each SSR class. 1=East, 2=South, 3=West, 4=North, 5=Cyclon, 6=Indifferent, 7=Anticyclon and 8=Mixed.

Different methods that made used of a combination of weather conditions and trajectories analysis were applied in the last sections to better understand the positive correlation between residence time and ozone found during summer. With this latter analysis various factors important for ozone production could be better quantified, but the results were affected by the relatively small amount of data.

8 Summary and Conclusion

Trace gases were measured at the alpine site Arosa (Switzerland) in an extended field campaign from September 2000 to August 2002. The measurements were performed about 150 m above the village of Arosa at an altitude of 2035 m (asl). Arosa is a site which is not directly exposed to the synoptic circulation as it is surrounded by mountain peaks ranging up to 2500 - 3000 m. In the valley leading to Arosa a typical valley wind circulation develops with upslope and upvalley winds during day time and downslope and downvalley wind at night. The chemical data set (O_3, NO_y, CO, NO_x) showed a high degree of variability with respect to season, different weather conditions and related transport processes. This variability was analysed in different case studies including single events and more extended periods providing a consistent picture on the trace gas behaviour in Arosa.

Ozone measurement revealed a ***seasonal variation*** similar to other sites in central Europe (spring maximum, followed by enhanced concentration in summer and a minimum in fall). In contrast NO_y concentrations did not show any particular seasonal variation and indicated, together with the NO measurement, that Arosa was under the influence of local emissions from the village throughout the year. This local influence was mainly restricted to day-time during upslope conditions and most pronounced in the winter time during the ski season.

The analysis of the averaged ***diurnal variation*** in trace gases concentrations revealed distinct differences in their dependence on the season and on the weather conditions.

In ***winter*** ozone showed only a weak diurnal variation. The highest ozone concentrations were reached in early morning during fair weather days, i.e. at the end of the valley outflow phase. At the same time the lowest NO_y concentrations were observed. NO_y showed a pronounced diurnal variation on these fair weather days. After the minimum at morning time its concentration significantly increased due to local emissions and decreased to a lower value only in the late afternoon with the starting of valley outflow phase. These days with fair weather were mainly characterised by anticyclonic conditions and strong temperature inversion. A comparison between Arosa and Jungfraujoch (3578 m asl) indicated that Arosa can not be considered as regularly exposed to the free troposphere. During the wettest days typically characterised by advective weather ozone concentration in Arosa decreased much strongly than at Jungfraujoch showing that Arosa was more influenced by such weather change and more exposed to ozone-poor air transported from the boundary layer. Closely similar variations were found in ***fall***.

The transition to warmer season revealed interesting features about ozone in relation to changes in solar radiation and in meteorological transport processes. In ***spring*** ozone maximum peak often occurred during afternoon highlighting the contribution of local photochemical activity in increasing the ozone budget in Arosa during this season. During ***summer*** fair weather days photochemical activity caused increases in ozone and in NO_y concentrations leading to their highest values recorded within this season. An ozone decrease quickly took place as morning upslope winds started to transport air from lower altitude more subjected to dry deposition and titration by local emitted NO. Thereafter ozone gradually increased again interestingly touching its maximal peak after sunset. At this moment of the day high remaining NO_y and CO concentrations provided evidence that the valley outflow at night is associated with

advection of photochemically well processed air to the site of measurement. This trace gas behaviour was found to be in strong contrast with the one described for Jungfraujoch. At this site a clearly detectable afternoon maximal peak in NO_y and CO, caused by convection of air from the boundary layer, was followed by advection of clean free troposphere influenced air. This clearly underlines that the boundary layer, at least in the mountain region, can easily reach altitudes up to 2000 m (asl) during summer fair weather days. This kind of boundary layer influence in Arosa appeared during day time directly through upslope conditions and indirectly at night by transport from the residual layer.

Against the expectations before the campaign, chemical measurements revealed that the site of Arosa can not be considered as being exposed to the free troposphere unless during very special events in winter. An event in November 2001 characterised by extremely strong inversion regime and strong subsidence over the alpine area shows very similar NO_y and ozone concentrations together with a comparable low value in the NO_x/NO_y ratio at night and early morning.

In winter time the ozone concentration in Arosa was found to be mainly influenced by the alternation of advective weather and high pressure situations. High ozone concentrations were found during periods characterised by a ***temperature inversion*** uncoupling the measurement station from the pollutant source regions at low altitude whereas very low ozone concentrations were associated with transport of ozone poor air from the boundary layer, often during uplifting ahead a ***frontal system***. A spectacular and exceptional event registered in Arosa and at Jungfraujoch in November 2001 showed that extremely low ozone and high primary pollutants concentrations can also be caused by transport processes other than uplifting ahead a frontal system. In this occasion polluted air masses previously uplifted at high altitude by a front were horizontally advected to the Jungfraujoch several hours later.

The positive correlation found for ozone and ***temperature differences between Arosa and Chur*** could be mainly explained by temperature inversion regime and advective weather. A comparison with Payerne meteorological sounding revealed that a temperature difference between Arosa and Chur can be used as an estimate for selecting days with inversion located over the Swiss Plateau below 2000 m (asl). Averaged vertical ozone profiles constructed with measurements from NABEL network showed that the alternation between days with and days without inversion regime affects the troposphere up to an altitude of 3500 – 4000 m (asl). The magnitude of this influence was further found to be comparable for stations located in the boundary layer and mountain stations normally located above the inversion layer. The analysis on the profiles could be further investigated. In particular comparison with Payerne ozone sounding could show if similar profiles are also confirmed above a flat and opened terrain. Ozone sounding could possibly reveal the stronger effect of alpine orography in uplifting ozone-poor air from the boundary layer into the lower free troposphere.

Transport of gas pollutants on a regional scale towards the Alps became evident in the analysis of ***south foehn***. In agreement with previous studies the Po basin was identified as a strongly polluted area. This work could additionally demonstrate how foehn flow can obviously descend to the Arosa basin when passing the Alps. Single cases and climatology revealed that in summer and in spring foehn was often related with enhanced ozone and NO_y concentrations. At the lower altitude station Chur (560 m asl) the foehn was instead found to occur less frequently but to have a stronger influence throughout the year. Backward ECMWF trajectories ending in Arosa

described the motion over the Po basin and indicated that the transport occurred usually fast but not necessarily at very low altitude in agreement with previous studies. A comparison between Arosa and Mt. Cimone (2165 m asl) revealed how accumulation of photochemically produced ozone can occur in an air parcel moving over the Po basin during foehn events in the warm season. The increase in ozone between both stations was on average more important for foehn events characterised by an air parcel passage over the Po basin occurring during day time and resulted in high ozone concentration in Arosa. This comparison analysis suggests the possible relevance of an air parcel passage over the Po basin during the photochemically active part of the day. It could be possible to further extend this analysis by comparing the results based on measurements in Arosa and Mt. Cimone with values calculated with a photochemical box model. The effect of ozone titration and/or dilution with ozone-poor air from the boundary layer over the Po basin could instead explain the negative difference in ozone between Arosa and Mt. Cimone calculated for events occurring in the cold season. This type of comparison could provide an additional tool for further investigate the interactions between foehn flow and boundary layer over the Po basin which are not well known at present. Detailed information of the boundary layer structure over the Po basin would be also a requirement. A preliminary comparison between maximal pressure of ECMWF trajectory over the Po basin with ozone concentration and ozone difference between Mt. Cimone and Arosa did not yield any valuable result. The application of trajectory from mesoscale models (e.g. Local Model of Meteo Swiss) could possibly do a better job in resolving the vertical motion relatively close to the Alps.

No correlation was found in summer and in spring by comparing ozone concentration in Arosa during ***foehn events*** with ***residence time of air parcel over Europe***. Thus the very long history of an air parcel seems not to be important for the ozone in Arosa when a passage over the Po basin occurs.

During a prolonged fair weather period in ***summer*** characterised by **high pressure** the day after day increase in ozone concentration in Arosa was found to be only slightly lower than in sites much more closely located to emission sources such as the rural site Taenikon (538 m). A striking increase was also found at the high alpine station Jungfraujoch. Such events in alpine areas characterized by strong convection obtained recently scientific attention as sources of venting of (polluted) boundary layer air into the lower free troposphere. The large scale motion from high altitude and high latitude determined a strong decrease in ozone concentration down to 2000 m. These **low ozone concentration** should not be compared with the low ozone concentration found during or immediately after a front passage as these are mainly determined by loss processes occurring in the lower troposphere.

The generalisation of the ***emission-receptor relation*** is a challenging task. This is in particular true for a site located in the middle of the continent which is normally not exposed to a clean sector opposite to a clearly polluted sector as e.g. a coastal site. Therefore it was considered useful to apply the method of Pochanart *et al.* (2001) that compares the residence time of polluted air masses over the European continent with ozone concentration at the receptor site in Arosa. According to this model ozone concentration is expected to increase with every additional day residence time over Europe. The application of this kind of analysis yielded in summer only weak correlations. Weather conditions and differently polluted area within the continent are major factors that the quantity “residence time” can not account for.

An agreement with Pochanart et al. (2001) is nevertheless achieved if residence time classes are introduced yielding a positive trend from March to September (excluded May). However the method does not appear to be sufficiently appropriate to estimate the **hemispheric ozone background** since low ozone concentrations in Arosa are found to be mainly determined by loss processes occurring in days characterised by a frontal passage.

Alternative approaches revealed that a positive relationship between residence time and ozone concentration is usually restricted to **fair weather conditions**. The strongly positive correlations found in June and July during anticyclonic weather events revealed that these events were important for the positive tendency found between ozone and residence time during these two months. A detailed analysis restricted to two of these events suggested once again that the reminiscence of bad weather and the air parcel passage over a highly polluted area such as the Po basin are additional factors that the residence time can not perceive although they might influence the correlation. The positive correlation between residence time and ozone concentration found from May to July for the driest days in Arosa suggested that an accumulation takes place only on days with the most favourable conditions along the trajectories. No peculiar tendency was observed during the most humid days. More convincing results were obtained for June and July when surface solar radiation from the ECMWF fields were assessed along the trajectories. Despite the coarse resolution of the fields these radiation data yielded a good separation of ozone measurements providing indirectly evidence that this tool could be used to separate days with good weather conditions along the trajectories from days characterised by typically bad weather conditions along the trajectories. A further investigation used NO_y as a tracer for NO_x emissions during fair weather and confirmed that both radiation and pollutant emissions on a regional-continental scale are important factors to be considered for the understanding of (high) ozone concentrations in Arosa during summer.

The general strength of the residence time analysis is that it is relatively simple, also in its implementation. The main weakness is that the results and the limitations of the method can hardly be improved, for example, by a better parameterisation of processes important for ambient air concentration such as photochemical reactions, cloud coverage, pollutants deposition or pollutants emission. Three dimensional (mesoscale) atmosphere-chemistry models are often used to overcome this problem and can explain reasonably well the trace gases distribution in the atmosphere (Langmann, 2000). Another factor influencing the emission – receptor relation, upon which attention is raising more and more, is the intercontinental transport of pollutants which is mainly investigated by global chemistry transport model (Li *et al.*, 2002; Stohl *et al.*, 2002).

Finally it is sensible to advance general technical considerations on the difficulties concerning trace gas measurements. For ***extended measurements*** the maintenance of the instruments should not be underestimated. For this purpose the remote control of most of the instruments of the station proved to be useful as failure were relatively fast discovered and allowed fast reparation when necessary. For future applications it is recommended that the station should have an easy access. Further it would be very useful to have a trained person, especially for extended measurements at stations located far away, which could fast intervene in case of not too serious problems or unexpected basic maintenance work. In any cases one should be aware that a control of the station by a qualified person every 1 or 2 weeks is indispensable in order to provide good measurements.

The data of the trace gases measurements performed in Arosa are stored on a CD-ROM and freely available for further investigation. The CD-ROM contains in addition to the O_3, NO_y, NO_x and CO also VOC data obtained by Li (2003). The data is archived as hourly average (CET).

Appendix

A.1 Synoptic weather classification by Schüepp

A.1.1 Chemical measurement in Arosa and synoptic weather

The entire data set was compared with the synoptic weather classification by Schüepp. The analysis shows that the relation between pollutants concentrations and synoptic weather type is often weak not allowing significant separation. Figure 85 shows box plots for the months November and December respectively June and July whicc are the months showing the most significant results.

During the cold season from October to February the weather classification by Shüepp can obviously not explain the variability in ozone concentration. Similar results are found for NO_y, slightly lower (median) values for anticyclonic and indifferent weather conditions in November - December. During the warm season a better separation is found for ozone which usually shows the highest ozone values on days with anticyclonic and indifferent weather conditions. This tendency is to explain with the enhanced photochemical activity during these weather types but is most pronounced only in June - July. Similarly NO_y is often found to be highest during fair weather types (anticyclonic and indifferent), beside photochemistry this finding can be understood as a better developed valley wind circulation which finally results in a more efficient vertical transport of pollutants from the boundary layer. Within the advective weather types lower ozone and NO_y concentrations are found (for median value) for northerly and westerly advection. This is related to the meteorological conditions which are less favorable for photochemistry and more favorable for (wet) deposition (low radiation, high humidity) during such weather types, whereas slightly higher values are found for S advection.

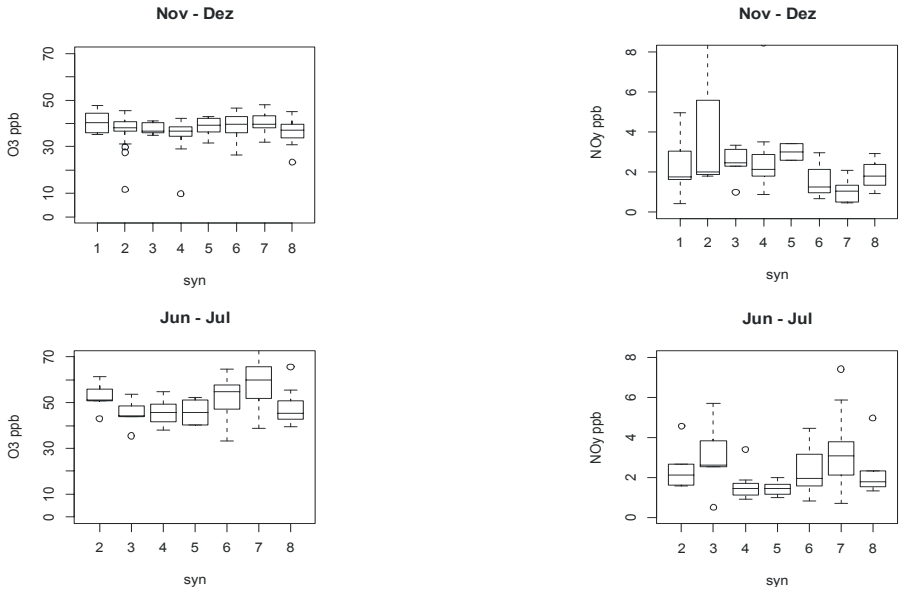


Figure 85: Boxplot of ozone and NO_y concentration in Arosa with respect to the extended weather types 1=East, 2=South, 3=West, 4=North, 5=Cyclon, 6=Indifferent, 7=Anticyclon and 8=Mixed (daily measurements between 20 and 06 CET are used).

Reasons for this weak separation are certainly found in the position of Arosa, in the middle of central Europe not exposed e.g. to a clearly clean sector in opposition to a clearly polluted sector as a coastal side like Mace Head in Ireland (Monks, 2002) or Norfolk in the UK (Harrison *et al.*, 2000). The resolution of this classification (1 day) can not always describe the changes in meteorology that might occur in a shorter time scale (e.g. front passage or a south foehn). In addition the long history of an air mass is only partially considered. Indifferent weather was e.g. observed to occur during very different situation such temperature inversion regime, frontal passage and south foehn event. Similarly south foehn events were found during different synoptic weather types (see also section 5.3.3).

Next it is focused on the most clean and on the most polluted days in Arosa and their dependence on the synoptic weather type is investigated.

A.1.2 Occurrence of clean and polluted days in Arosa and Taenikon

To define clean and polluted days the daily mean of NO_y concentration in Arosa and the daily mean of NO_x in Taenikon were used. At Taenikon NO_y is not measured, the NO_x measurement suffers however from cross sensitivities to other nitrogen compounds and thus represent more NO_y than NO_x (Bronnimann, 1999). Class I (clean days) contains 30% of the days with the smallest NO_x/NO_y concentrations, in class II (polluted days) were included 30% of the days with the largest concentrations. Figure 86 shows the seasonal variation of concentrations of clean and polluted days at the two locations and includes for each season about 55 days. Climatological season were used. Compared to class I (clean days) the higher NO_y values in Arosa in class II (polluted days) are connected with higher O_3 concentration in spring (+6.3 ppb) and summer (+11.6 ppb) and lower O_3 concentrations in winter (-3.8 ppb) and fall (-4.1 ppb). This result can be explained by photochemistry in spring and summer and O_3 loss due to titration and deposition in winter and fall (-4.1). In Arosa the spring maximum (50.8 ppb) appears in class I whereas in class II similar values are reached also during summer time.

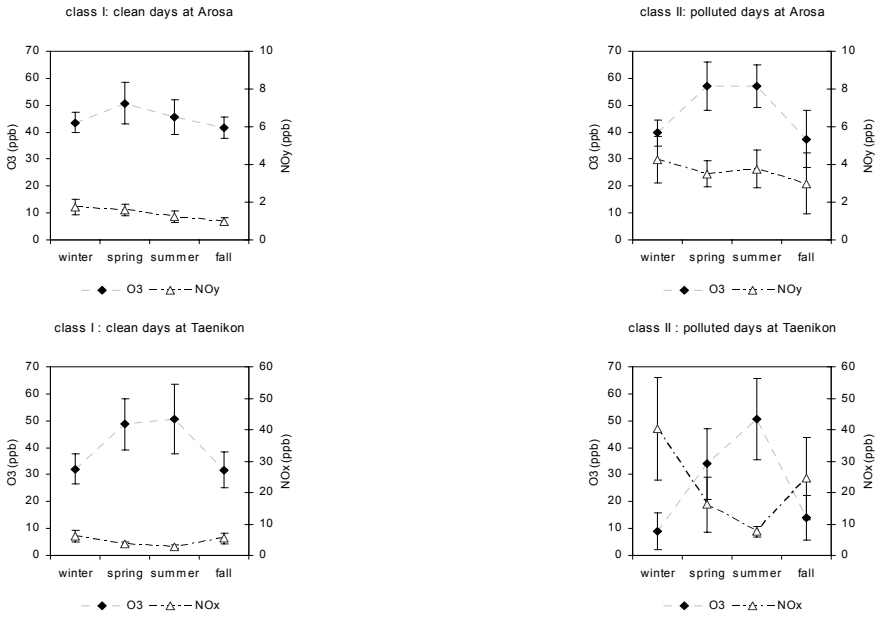


Figure 86: Ozone and NO_y concentration on clean and polluted days in Arosa (top), ozone and NO_x concentration on clean and polluted days at Taenikon, compare text for definition. Winter: DJF, spring: MAM, summer JJA, fall: SON.

At Taenikon higher NO_x concentration were always connected with low ozone concentrations except in summer. The differences in ozone between class I and class II in winter (-17.6 ppb), fall (-22.9 ppb) and spring (-14.7) suggest that ozone can be to a large extent titrated by fresh (NO) emissions. Note that for Taenikon only ozone measurements during day time (between 10 and 18 CET) were used. In summer O_3 concentration was instead higher for polluted days than for clean days (+9.2 ppb). In a first attempt using the ozone measurements of the entire day no difference was found in ozone concentration in summer in the two classes (ca. 38 ppb in both classes) which show how strongly loss processes at night can influence ozone concentration at Taenikon. The higher O_3 concentrations in class II in summer at Taenikon and in Arosa can be regarded as the effect of the general summerly NO_x limited O_3 formation in rural Switzerland (Staffelbach & Neftel, 1997). At Taenikon the spring maximum was just recognizable for clean days (48.7 ppb) and clearly disappeared for polluted days. O_3 concentrations at Taenikon and Arosa strongly differ to each other for polluted days in winter (-30.6 ppb) spring (-23.1 ppb) and fall (-23.4 ppb) whereas are more similar only in summer (-1.43 ppb). Ozone concentrations at the two sides are instead much more similar all of the year for clean days.

This result is plausible as ozone concentration within class I can be regarded as a very simple estimate for background condition.

Figure 87 shows the frequency of the 8 synoptic weather types for clean and polluted days. Days with very low pollutant concentrations (clean days) clearly occurred in Arosa and Taenikon at different weather conditions in winter. In Arosa anticyclonic and indifferent weather conditions were prevailing during such periods (60%), in Taenikon the advective weather types were instead most frequent (74.5%). These two completely different behaviors are related to the altitude of the stations. In case of high pressure conditions Taenikon is most of the time below a temperature inversion layer. When during such cases accumulation of NO_x occurs one efficient way to reduce their concentration is given by (strong) advection possibly connected with a front passage. A similar pattern even if less pronounced is observed in fall.

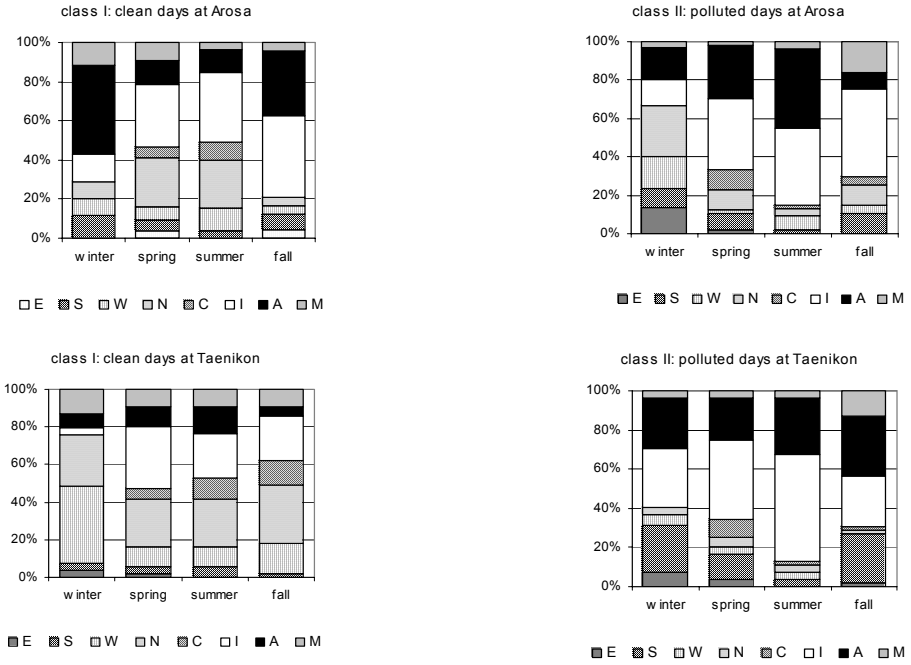


Figure 87: Frequency of the synoptic weather types for clean and polluted days in Arosa (top) and Taenikon (bottom).

Results in spring and summer at both sites do not differ within class I at both sites and indicate that convective and advective weather occurred almost with the same frequency. Within the advective weather types N and W are more frequent and represent a not negligible amount of clean days. For polluted days the frequency of convective conditions is obvious at Taenikon through all the year and in Arosa in summer and partly in spring. Lack of advection and high atmospheric stability are favorable for accumulation of primary pollutants on the Swiss Plateau whereas in the alpine valley the high solar radiation (in summer) induces a strong valley wind circulation which is favorable for vertical transport of pollutant from the boundary layer up to higher altitudes. In winter in Arosa, highest pollutants are instead mostly found during advective weather which is related to the break up of the inversion layer and the following vertical transport of pollutants. In fall in Arosa a similar, but less pronounced, tendency as in winter is observed. In Figure 88 the ozone values depicted in Figure 86 are further separated according to the weather type (note the different axis in class II at Taenikon).

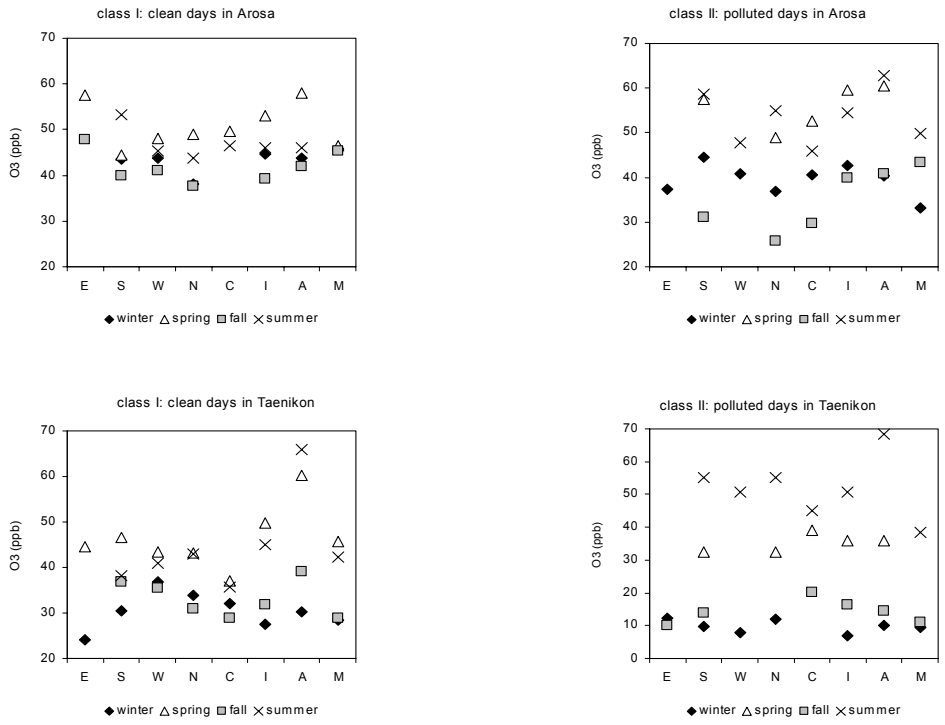


Figure 88: Ozone concentration for clean and polluted days in Arosa and Taenikon and their seasonal variation within the 8 weather types (data are rapresented if measurements during at least 72 hours are available).

For clean days the spring maximum is evident in Arosa in all weather classes except for South advection. In case of south advection substantially higher concentration are found in summer. During anticyclonic weather the highest ozone concentrations in spring are obvious. In Taenikon the spring maximum within class I is less pronounced. As soon as meteorological conditions are most favorable for O_3 production enhanced ozone concentrations are found at Taenikon (anticyclonic weather in spring and summer). The seasonal differences within a single weather type for clean days are generally found to be smaller than for polluted days at both locations. The smallest differences are found in air masses associated with westerly advection in class I. This result is plausible considering that these air masses often originate from the (less polluted) Atlantic region, traveling relatively fast over the European continent and are associated with high humidity and lower radiation which inhibit the photochemical ozone production in summer. Moreover ozone concentrations at both sites are on average during westerly advection more similar to each other than in other weather types (e.g. in spring 43.4 ppb at Taenikon and 48.0 ppb in Arosa, in summer 40.8 ppb at Taenikon and 45.3 ppb in Arosa). It is interesting to note that for clean days with anticyclonic weather O_3 in Arosa does not differ too much from each other in summer, winter and fall (between 42 and 46 ppb). This weather type in summer is generally associated with low pollutants shortly after a bad weather period. In this case ozone concentrations are low, i.e. influenced by the weather found the previous days. This is the most probable explanation for the low O_3 concentrations found in class I. The NO_x limitation of O_3 production at rural sites (Staffelbach & Neftel, 1997) and the O_3 destruction in very remote area (Bremaud & Taupin, 1998; Solberg *et al.*, 1997)are also possible reasons for low ozone concentration in summer but are not supposed to play a role in this case. A large separation of ozone concentration is achieved for polluted days in every weather type which underlines again the role played by NO_x in the ozone regime at both stations. It was already reported above about westerly advection being responsible for fast transport of air masses from the Atlantic region. Figure 89 shows the comparison between air masses residence time over Europe calculated by backward trajectories ending in Arosa and the synoptic weather classification.

In every class a very large variability in residence time is found indicating that there is hardly a generally valid relation between both quantities. On average smallest residence time are recorded for westerly or northerly advection (< 2 days for median value), whereas largest residence times (median)

were found for the convective weather types (anticyclonic, indifferent and cyclonic) and the rather seldom E advection. Large residence times in case e.g. of westerly or northerly advection are related with different synoptic conditions prior to the classification into the synoptic classes. Indeed the synoptic classification only takes into account the weather conditions at one specific day whereas the residence time also includes information about previous days.

In this section we compared the synoptical weather classification by Schüepp with Arosa measurements, at the end of section A.1.1 it was already reported about reasons leading to a weak separation of NO_y and ozone measurement. With the analysis applied to polluted and clean days more results were obtained. A main disadvantage of the analysis was the limited dataset (2 years). The availability of a larger data set would have most probably not provided better results; such an extended analysis is not recommended.

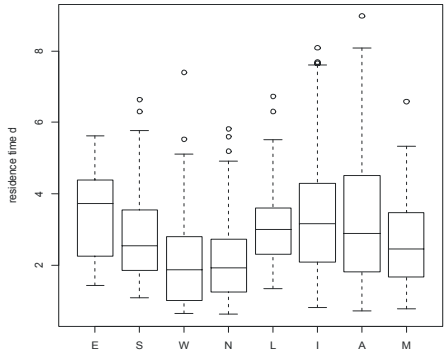


Figure 89: Boxplot of residence time over Europe of air masses calculated from 10 days backward trajectories ending in Arosa with respect to the different weather types (E=East, S=South, W=West, N=North, L=Cyclon, I=Indifferent, A=Anticyclon and M=Mixed, daily measurement two year, ca. 700 trajectories).

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