Tropospheric carboxylic acids in tropical rainforest environments :

a study of their presence in the gaseous and aqueous phases under maritime to continental transport regimes.

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Jaime F. Quesada-Kimzey

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Abstract

The eastern coasts of tropical areas are witness to the transition of the marine boundary layer to a continental boundary layer. Two field campaigns were conducted in forested tropical areas with a marine boundary layer being advected inland over the forest. The first of these took place in the northeastern plains of Costa Rica, during July 1996; the second was led in the flat and forested Surinam, in the general framework of the Cooperative LBA Airborne Regional Experiment (CLAIRE) campaign, in March 1998. Organic acids, produced by oxidation of hydrocarbons in the atmosphere, were chosen as the key trace gases to be quantified in order to examine this transition.

In the Northeastern plains of Costa Rica (*ca.* 10°25' N; 84°W), rainwater was sampled from July 08 to July 29, 1996. It rained in average 220 mm in the area, and over 500 samples were collected. The sampling sites were located approximately along the wind direction at 1, 20, 60, 60 and 80 km from the coast. Complementary instruments were an ozonemeter and a meteorological station; both were operated 60 km inland. The collected samples were preserved, frozen and later analyzed for carboxylates, inorganic anions, Ca²⁺, K⁺, NH₄⁺ and Mg²⁺. The mean boundary layer windspeed was *ca.* 5 ms⁻¹ from the NE.

Site specific volume weighted average concentrations of main analytes were between 2.7 and 4 μ M formate, between 1.5 and 2.2 μ M acetate, between 20 and 32 μ M NaCl, between 2.8 and 3.3 μ M SO₄²⁻, between 4.6 and 8.3 μ M NO₃⁻, between 3.1 and 9.6 μ M H⁺, and between 5.3 and 9.5 μ M NH₄⁺. Seasalt components Na⁺, Cl⁻ and Mg²⁺ and seasalt SO₄²⁻ showed mean loss rates with distance from the coast of *ca*. 0.4% km⁻¹; total SO₄²⁻ showed a decrease rate of about 0.2% km⁻¹. Land surface related species Ca²⁺, K⁺, NH₄⁺ and NO₃⁻ showed mean increase rates with distance from the coast of 1.1 % km⁻¹, 0.7 % km⁻¹, 0.4 % km⁻¹ and 0.5 % km⁻¹ respectively. For the organic acids neither an increase nor a decrease with distance from the coast of search and search are nor a decrease with distance from the coast of normal search are normal search are search and 0.5 % km⁻¹ respectively. For the organic acids neither an increase normal search are search and search are search and search are normal search are normal search are search and 0.5 % km⁻¹ respectively. For the organic acids neither an increase normal search are search and search are search and search are normal search are normal search and search are search and search are normal search are search and search are search and search are normal search are normal search are normal search are search and search are search are search are normal search are search are search and search are searc

Loss rates of gas phase HCOOH and CH₃COOH in the mixing layer by dry deposition were roughly estimated in 22 pmol mol⁻¹ h⁻¹ each during the daytime, equivalent to 10 μ mol m⁻² day⁻¹ each. Average wet deposition during the rainy part of the sampling period was estimated in *ca*. 45 μ mol m⁻² day⁻¹ formate and *ca*. 25 μ mol m⁻² day⁻¹ acetate, several times the estimated loss by dry deposition. It has been concluded that locally occurring contributions to the HCOOH and CH₃COOH gas phase mixing ratios in the area approximately equalled the losses by dry deposition, and that imports and local production by reactions were likely the major contributing processes to the local organic acids levels. The measured wet deposition of HCOOH and CH₃COOH implies the area to have been a net sink for these two gases in the mixing layer during the sampling period, rather than a source, as originally expected.

At the innermost site, enrichment of Ca^{2+} in rainwater with respect to the other sites was observed; it was coincident with a sharp decrease in H⁺ content and a depletion of formate apparently related to pH, which probably took place via reaction of formate ion with HO radicals. Long range transport of dust in the free troposphere is discussed as a possible mechanism originating the Ca²⁺ enrichment at the innermost site.

Formate and acetate contents were highly correlated at all sites, and the day to day variation of their ratio was observed to be very similar to that of the ozone afternoon mean. Additionally, the formate / acetate ratio was found to vary linearly with H^+ content in the samples, including the site where Ca^{2+} enrichment and related neutralization was observed. The relationships of the formate / acetate ratio with sample acidity and with the O₃ levels are discussed.

The O_3 afternoon averages in C.R. were between 7 and 17 nmol mol⁻¹, and the overall average was 12 nmol mol⁻¹. Day to day variations of O_3 afternoon averages and their similarity to variations of formate / acetate volume weighted average ratios are briefly discussed as a possible indicator of long range transport of O_3 and the organic acids towards the area. The organic acids in the mixing layer over the sampling area are concluded to have been imported, as well as O_3 and possibly a good part of the non seasalt components.

Compositional variation of the rainwater within individual events was examined, as several successive samples were collected during each event. Variation patterns observed by other workers in similar experiments were not observed in this case. The cause for this may have been a smaller effect of solutes scavenging in the under cloud air column, due to air in this work being mostly marine boundary layer air, therefore comparatively clean.

In Surinam, ground based measurements of gas phase organic acids, ozone and CO were led in Sipaliwini (2°02' N, 56°08' W), from March 13 through 27, 1998. The site was approximately 550 km downwind from the coast. Dry weather conditions prevailed, and the mean boundary layer wind speed was about 8 ms⁻¹ from the NE. From complementary airborne data, afternoon mixing layer depth (Z_i) was estimated in *ca*. 600 m near the coast, *ca*. 800 m about 50 km inland and *ca*. 1400 m at Sipaliwini, with an increase rate of *ca*. 3.6 m km⁻¹ near the coast. The depth of the nocturnal boundary layer was not estimated, so reference to other works in similar environments is made.

The general dynamics of the boundary layer and lower free troposphere are discussed in relation to the variations in the trace gas levels and their budgets. Consideration of advection of air masses above the nocturnal boundary layer leads to conclude that the air entrained into the mixing layer every morning after breakdown of the nocturnal boundary layer had no recent previous contact to the land surface of the continent. According to the estimates, the longest period of contact to the land surface that the air in the mixing layer in Sipaliwini could achieve was about 10 hours. The diel cycles of CO, O₃, HCOOH and CH₃COOH are presented and discussed, as well as the variations of their afternoon average mixing ratios during the sampling period. Data from other sampling sites operated by other groups near the coastline are presented as well and discussed.

CO average afternoon mixing ratios were mostly between 90 and 150 nmol mol⁻¹; the overall average of the afternoon values was 123 nmol mol⁻¹. Conclusive evidence of CO production due to oxidation of locally emitted volatile organic compounds (VOCs) was not achieved; variability of the CO level in terms of 10 hours was found to be similar to the increase that could have been expected for the same period at a fixed site, according to estimates made from airborne data.

 O_3 average afternoon mixing ratios varied between 11 and 19 nmol mol⁻¹; the overall average of the afternoon values was 11 nmol mol⁻¹. The net local loss rate of O_3 was estimated in *ca*. 5 %h⁻¹ during the afternoon hours. Several local loss processes for O_3 were roughly calculated and their sum was similar to the observed net loss rate. Deposition was found to be the major O_3 loss mechanism. Oxidation of VOCs in the local mixing layer was concluded not to have been ozone productive as far as Sipaliwini.

The major organic acids found in the gas phase were formic (HCOOH) and acetic (CH₃COOH). The average afternoon mixing ratios of HCOOH varied between 0.56 and 2.45 nmol mol⁻¹, with an overall average of the afternoon values of 1.2 nmol mol⁻¹. For CH₃COOH, the average afternoon mixing ratios varied between 0.62 and 1.45 nmol mol⁻¹, and the overall average of the afternoon values was 1.0 nmol mol⁻¹. The budgets of formic and acetic acids in Sipaliwini are discussed, arriving to the conclusions that downmixing of residual layer and of free tropospheric air were their major source process for the local mixing layer, and that local production by reaction played a secondary role, while primary emission probably did not make any significant contribution.

Based on the discussion of the boundary layer dynamics and on several other observations, it is concluded that, as far as Sipaliwini, the major source process of O_3 , CO and the organic acids for each day's mixing layer was the entrainment of marine boundary layer air and free tropospheric air that had been advected inland above the previous night's nocturnal boundary layer. Probably, one important mechanism leading to long range transport of the species under study was the advection of contaminated continental boundary layers over the ocean surface from Northern Africa, Southern Europe and possibly North America.

As a general conclusion based on the results of both field experiments, it is proposed that in pristine forested eastern tropical coastal regions as those investigated in this work, secondary species as O_3 , CO and organic acids are mostly imported in the marine boundary layer and in fossile continental boundary layers contained in the free troposphere, advected above the ocean, often from oveseas. Regarding organic acids, rainy conditions apparently could ensure that such areas represent net sinks for them. These two are aspects that do not seem to have been considered or directly addressed in the consulted literature.

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I INTRODUCTION

The occurrence and role of carboxylic acids in the atmosphere and its chemistry have been studied with growing interest in the last 15 to 20 years. Results of the diverse studies have revealed not only their ubiquity, but also some of the tropospheric chemistry they are involved in. In the tropical troposphere, organic acids can be the major acidification sources for cloud water and wet deposition in remote areas (e.g., Whelpdale et al., 1997 and references therein) and at the same time represent up to 10% or more of the gaseous NMHC concentrations. Low vapor pressure organic acids have been proposed to potentially play a role in gas to particle conversion processes (e.g., Lawrence and Koutrakis, 1996; Kubátová et al., 2000); they thereby acquire significance in cloud nucleation processes. In-cloud oxidation processes catalyzed by transition metal cations has been proposed to strongly depend on the presence of carboxylates (e.g. Zuo and Hoigne, 1992 and 1994; Greic et al., 1998). It has been proposed that as much as 30% of tropospheric O₃ destruction in some areas could be due to in-cloud processes involving formation of HO₂ and O₂⁻ radicals (Jonson and Isaksen, 1993), which in turn involves the complexing action of organic acids on transition metal cations; the issue, however, remains a matter of discussion (Lelieveld and Crutzen, 1991; Liang and Jacob, 1997). Finally, organic acids -in particular formic and acetic- in the boundary layer are an important one of several final stages in the gas phase oxidation of naturally emitted and anthropogenic VOCs, due to their fast dry and wet deposition rates.

Several tens of carboxylic acids with diverse additional functional groups have been identified in atmospheric samples so far. Usually, those with higher vapor pressures are found in greater concentrations in the gas phase; among these, formic and acetic acid are, with rare exceptions, the most abundant in the gaseous and aqueous phases. Dicarboxylic acids and long chain monocarboxylic acids have mostly been identified in aerosol and rainwater samples (*e.g.* Lawrence and Koutrakis, 1996; Kawamura et al., 1996 a,b,c; Kubátová et al., 2000). Specific organic acids derived from the oxidation reactions of monoterpenes have been identified recently in particles originating from gas to particle conversion (*e.g.* Dekermenjian et al., 1999; Yu et al., 1999). Acids with oxo groups (carbonyl) and double bonds originate from the atmospheric oxidation of diverse natural and

anthropogenic olefines. Oxoacids are frequently prone to photolysis in the gas phase, as is the case of pyruvic acid (2-oxopropanoic), with a lifetime of a few hours during daytime (Grosjean, 1983).

The presence of carboxylic acids varies qualitatively and quantitatively according to the different environments. The remote marine boundary layer is considered to have the lowest levels of organic acids overall, with concentrations frequently in the order of several tens of pmol mol⁻¹ (*e.g.* Keene and Galloway, 1988; Arlander et al., 1990; Talbot et al., 1999), including only formic and acetic acids in measurable amounts.

Tropical rainforest environments, in particular the large Amazon basin region, are considered to be among the most productive ecosystems on our planet and to represent a significant global atmospheric source of diverse trace gases. Formic and acetic acids have been measured in the gas phase of such environments, resulting in levels in the order of 1 nmol mol⁻¹ during the rainy season and up to *ca.* 15 nmol mol⁻¹ in the dry season (*e.g.* Talbot *et al.*, 1990; Andreae *et al.*, 1988a; Sanhueza *et al.*, 1992). Carboxylic acids may not be in first instance among the major exports of the tropical rainforests to the global atmosphere, due to their relatively short lifetime in the boundary layer, estimated to be of at most a few days, being deposition – wet and dry– their main loss channel (Keene and Galloway, 1988; Hartmann *et al.*, 1991). Nevertheless, they represent an important stage in diverse pathways of the oxidation of many naturally emitted and anthropogenic VOCs. Organic acids studied in tropical forest areas to this date include formic, acetic, pyruvic and a handful other less abundant species.

Polar environments also bear witness to the ubiquity of carboxylic acids. Kawamura *et al.* (1995 and 1996d) and Sempere *et al.* (1994 and 1996) have conducted saveral studies with samples from the Arctic and Antarctic. They have found several dicarboxylic and oxocarboxylic acids to significantly contribute to the polar organic aerosol and to the trace compounds in snow and ice. Apparently, several dicarboxylic acids are photochemically produced from contaminants transported from mid latitudes to the polar regions (Kawamura *et al.*, 1995). Urban and semiurban environments are reported with some of the highest levels and greatest diversities of carboxylic acids measured to this date (*e.g.*

Kawamura *et al.*, 1996 a,b,c; Grosjean, 1989 and 1990; Souza *et al.*, 1999). The predominance of formic and acetic acids is also the rule.

I.1.Sources

In current understanding, organic acids in the troposphere have a variety of known and suspected sources. Knowledge of the biogeochemical cycles of the tropospheric carboxylic acids is yet in a preliminary stage, and field results frequently cannot be justified satisfactorily in terms of source and sink processes (Talbot *et al.*, 1990; Chebbi and Carlier, 1996; E. Sanhueza, private communication, 1999). Some of the best known or most frequently invoked source processes of tropospheric carboxylic acids are shortly addressed in the following paragraphs; the first large division is into direct emission and formation from precursor species.

I.1.1.Primary emission.

I.1.1.1.Emissions by vegetation

Vegetation has long been a suspected primary source of atmospheric organic acids. One of the first published experiments to assess the emission of organic acids by vegetation in the field was carried out during the ABLE campaign (Talbot *et al.*, 1990). A bag enclosure was used to measure emissions from a branch. According to the results, plants could be directly involved in the emission of formic and acetic acids. The amounts produced, however, were estimated to be insignificant with respect to the budget in the local boundary layer. In a more recent publication, Bode *et al.* (1997) have estimated direct plant emissions to possibly represent a relevant part of the budgets of formic and acetic acids in the lower troposphere at a global scale. This paper is partly based on results of several enclosure studies made by the same research group involving several European species (*e g.* Hofmann *et al.*, 1997; Kesselmeier *et al.*, 1997 and 1998). More recent results involving several North American and European tree species have been published by Martin *et al.* (1999); in an enclosure study, several NMHC were measured along with formic and acetic acids; the latter represented between 1% and 12% of the total emitted mass of measured hydrocarbons.

With a different approach, Gabriel and collaborators (Gabriel, Doctoral Thesis, 1997; Gabriel *et al.*, 1996 and 1999; Gabriel and Kesselmeier, 1999) found correspondence between the measured emission of acetic acid and pH values and acetate concentrations in the apoplastic fluid of the plants. The acidity of the apoplastic fluid could, however, not justify the apparent emission of formic acid, which was measured along with acetic acid in the enclosure experiments. Increased osmotic pressure at the cell wall in the plant leaves during the afternoon hours, when insolation and temperatures are highest, has been proposed by Gabriel (Doctoral Thesis, 1997) as a likely cause for actual emission of formic acid. An important point that remains difficult to explain by this hypothesis is that formic acid was usually found in higher concentrations than acetic acid in the gas phase.

I.1.1.2.Soils

Savanna soils in Venezuela have been reported to be net emitters of formic and acetic acids at daytime during the dry season (Sanhueza and Andreae, 1991). But the estimated contribution to the boundary layer concentrations was in the order of 10 pmol mol⁻¹ day⁻¹ for both acids, which is little significant compared to usual boundary layer concentrations in the order of 0.5 to 5 nmol mol⁻¹.

I.1.1.3.The oceans

Because seawater is slightly basic (pH = -8), it acts as a sink rather than a direct source of acidic gases in the boundary layer. The marine boundary layer is generally considered to represent a net sink of carboxylic acids.

The oceans may, however, represent a source of precursor hydrocarbons (*e.g.* Keene and Galloway, 1988; Bonsang *et al.*, 1988 and 1992; Donahue and Perrin, 1993). Diverse hydrocarbons are apparently produced and released by marine microbiota; they migrate to the surface and finally evaporate or pass into the atmosphere on the seaspray. This indirect source, however, has only been related to low amplitude diel cycles and slightly elevated levels of organic acids and precursors occurring mostly during the latitudinal growth period (Arlander *et al.*, 1990) in the marine boundary layer, and probably lacks global relevance.

In other cases, events of higher levels of organic acids in the remote marine boundary layer, particularly acetic and formic acids, have been assigned to continental sources, mostly in

connection to smoke plumes from biomass burning (Talbot *et al.*, 1996 and 1997; Singh *et al.*, 1996; Mauzerall *et al.*,1998). The plumes were presumably advected in the continental boundary layer over the ocean; once there, part of the former continental boundary layer decoupled from the marine boundary layer. Thus, water soluble gases and particles were presumably preserved in the decoupled layer above the marine boundary layer, where their long range transport over the oceans took place. Entrainment and turbulent diffusion were presumably responsible for incorpoarating part of the decoupled layer into the marine boundary layer (*e g.* Talbot *et al.*, 1996 and 1997). Precursors advected into and remaining in the marine boundary layer are not discussed in these works as a likely important source of organic acids.

I.1.1.4.Biomass burning

Biomass burning is a major direct and indirect source of organic acids in vast areas of the world, among them the African continent, South America, Canada, and the Indian subcontinent. Biomass burning events are not necessarily man made; natural events are common in Canada and other subarctic regions, as well as in savanna areas. Nevertheless, biomass burning acquires much of its significance in its anthropogenic component. Marufu et al. (1999) have estimated emissions of acetic and formic acids from cooking fires in Zimbabwe to represent about 10-15% of the total NMHC emission. Biomass burning has been found in several studies to directly emit larger amounts (in the order of 10 times as much) of acetic acid than of formic acids (Talbot et al., 1988; Hartmann, 1990). Several field measurements involving relatively fresh biomass burning plumes have also given such results (e.g. Lefer et al., 1994; Lacaux et al., 1992a). Oher studies involving aged plumes (Talbot et al., 1996 and 1999) relate high levels of organic acids over the remote marine boundary layer to continental biomass burning emissions that were transported in the free troposphere. Formic acid was found in those cases to predominate over acetic acid. Similar results were obtained in aged smoke over land by Helas et al.(1992) and Sanhueza et al (1996b); secondary production of organic acids by oxidation reactions of the originally emitted hydrocarbons presumably led to larger production of formic acid.

I.1.1.5.Combustion of other fuels

Combustion of fuels in motors and industry represents an additional direct and indirect source of organic acids that is determinant for the urban and semiurban troposphere. Several works have shown that high concentrations of organic acids can be found in the motor exhaust of engines (*e.g.* Kawamura *et al.*, 1987; Talbot *et al.*, 1988). Satsumabayashi *et al.* (1988 and 1995) report on the formation of diverse organic acids by aging of Tokyo city emissions during long range transport of the urban plumes over central Japan. The global relevance of urban emissions regarding the carboxylic acids has not yet been addressed in the literature; it is, however, brought up by the studies of Sempere *et al.* (1996) and Kawamura *et al.* (1996c and d) involving organic acids in the polar regions that probably originate in the local photochemistry of contaminants imported from mid latitudes.

I.1.2. Chemical formation of tropospheric carboxylic acids in the gas phase.

In current understanding, there are three major general pathways by which carboxylic acids are produced in the tropical boundary layer. One of them is the reaction of peroxyacyl radicals with other peroxyl radicals, including HO₂. The ozonolysis of alkenes provides another important formation pathway. A third possible one is the aqueous phase oxidation of aldehydes. These are shortly addressed in the following paragraphs.

I.1.2.1.Ozonolysis of alkenes

Many anthropogenically and naturally emitted NMHCs are insaturated. Naturally emitted NMHCs, together with those originating in biomass burning, represent the most substantial part of the global production. Several overviews regarding biogenically emitted organic compounds (now often called BOVOCs) have appeared in recent years. Among them, that of Fehsenfeld *et al.* (1992) is one of the most comprehensive, while that of Kesselmeier and Staudt (1999) is one of the more recent ones. Insaturated hydrocarbons readily react with ozone in the gas phase, yielding as end products a carbonyl and a carboxylic acid, as summarized in RI-1.

 $R_aCH = CHR_b + O_3 \rightarrow R_aCHO + R_bCOOH$ RI-1 One of the important formation processes of formic acid in unpolluted environments is the ozonolysis of terminal alkenes (Neeb *et al.*,1997). Ozonolysis of higher alkenes can lead to formation of acetic acid, propionic and so on, depending on the position of the insaturation (Grosjean *et al.* 1994).

Isoprene (2-methyl-1-3-butadiene) emissions represent by far most of the identified biogenic directly emitted reduced carbon in the tropical and subtropical forested regions. It was among the most abundant NMHC species measured during the LBA-CLAIRE campaign (a part of which is presented in this work) in the boundary layer of Surinam, over the rainforest (Warneke, doctoral thesis, 1998). The two main initiators of isoprene oxidation in the unpolluted boundary layer are HO radical and O₃. Oxidation of isoprene and its products leads to the production of significant amounts of formic acid; Neeb *et al.* (1997) measured 5% (relative to O₃ consumption) direct production of HCOOH and *ca.* 30% additionally over initial formation of hydroxymethylhydroperoxide (HMHP), in ozonolysis of isoprene in presence of water vapor. HMHP can be photolyzed (Burrows *et al.*, 1989) to formic acid and HO₂ and it can also react with HO radicals to yield the same products, catalyzed by R-OO radicals (Vaghjiani and Ravishankara, 1989).

Further carboxylic acids formed by ozonolysis of isoprene are pyruvic (2-oxopropanoic) and methacrylic (2-methylpropenoic); pyruvic acid can also be formed by HO initiated oxidation of isoprene. While methacrylic acid has not yet been found in the field, pyruvic acid has been found in the gas, aqueous and particulate phases. The lifetime of methacrylic acid is presumably very short (Neeb *et al.*, 1998); that of pyruvic acid during the day is of a few hours, depending on the solar zenith, because it readily photolyzes in the troposphere (Grosjean, 1983). Reaction of pyruvic acid with HO radicals has been found to have negligible significance and dry deposition probably also plays a negligible role compared to photolysis (*ibid.*).

Other insaturated biogenic NMHCs as terpenes and some of their oxidation products can also undergo ozonolysis, conducing to formation of carboxylic acids in some cases. Some of them have been studied in laboratory experiments (Dekermenjian *et al.*, 1999) and in field measurements (Yu *et al.*, 1999).

I.1.2.2.Peroxyacyl radicals

The reactions of peroxyacyl radicals with other peroxy radicals are an important formation route for several carboxylic acids (Madronich *et al.*, 1990; Madronich and Calvert, 1990; Jacob and Wofsy, 1988). The major formation routes of acetic acid in lightly contaminated and clean atmospheres are, in current understanding, the reactions of acetylperoxy radicals with peroxy radicals (HO₂, RO₂), schematized in RI-2 and RI-3 ($k_2 = 4.3 \times 10^{-13} \exp((2100 \pm 1200)/T)$ cm³ molecule⁻¹ s⁻¹; $k_3 = (4.1\pm1.2)\times10^{-15} \exp((1040\pm100)/T)$ cm³ molecule⁻¹ s⁻¹) (Moortgat *et al.*, 1989a and 1989b). Peroxyacyl radicals can also self react, but the methylperoxy and the peroxy radicals are expected to be their main reaction partners. The oxidation reactions involving isoprene and some of its products can provide them in the necessary amounts.

$$CH_3CO(OO) + HO_2 \rightarrow CH_3CO(OOH) + O_2$$
 RI-2a

$$\rightarrow$$
 CH₃COOH + O₃ RI-2b

$$CH_3CO(OO) + H_3COO \rightarrow CH_3COO + O_2 + CH_3O$$
 RI-3a

 \rightarrow CH₃COOH + HCHO + O₂ RI-3b

Reaction RI-2a is the major one of the two RI-2 (*ca.* 70%), but the peroxyacetic acid readily decomposes or reacts to form acetic acid.

When higher levels of NO_x are present, reactions yielding peroxyacyl nitrates (PAN) (RI-4 and RI-5) and other nitrates become more important, and can be a significant loss pathway for the radicals. These organic nitrates are thermally unstable and higher temperatures can cause the reactions to occur in the opposite direction. For this reason, they play an important role in the long range transport of NO_x in the higher and cooler free troposphere. The role of PANs as sinks or sources of peroxyacyl radicals and ultimately of carboxylic acids, however, is probably minor, and in any case of less significance than their role in the NO_x and O₃ chemistry (Crutzen, 1979; Singh and Hanst, 1981).

$$RC(0)OO + NO_2 \rightarrow R-C(0)OONO_2 \qquad RI-4$$
$$RC(0)OO + NO \rightarrow RC(0)O + NO_2 \rightarrow R - C(0)ONO_2 \qquad RI-5$$

Peroxyacyl radicals can be formed by different processes, the major ones of which are photolyses of carbonyl compounds (RI-6, for example). Thermal decomposition of PANs represent another formation pathway, though a minor one. The presence of significant amounts of acetone (Poeschl *et al.*, 2001) in the tropical troposphere can imply an important reservoir of peroxyacetyl radicals, from which acetic acid can ultimately be produced.

R-COCH₃ + hv + 2 O₂ → ROO + CH₃C(O)OO ($\lambda < ca.$ 320 nm) RI-6

I.1.3. Chemical formation of tropospheric carboxylic acids in the aqueous phase.

In-cloud aqueous phase oxidation by HO radicals of acetaldehyde has been estimated to be too slow to be of significance in the formation of acetic acid in the Amazonian boundary layer (Talbot *et al.*, 1990). With formaldehyde, on the other hand, this is likely to be a significant HCOOH production pathway, as long as the pH in the droplets is close to 4 or below. In that case, evaporation of the formic acid and enhancement of the gas phase concentrations occur. Contrariwise, at pH ≥ 5 , cloud chemistry should represent a net sink of formic acid by means of the reaction of formate anion with the HO radical to CO₂ (Chameides and Davis, 1983; Chameides, 1984).

I.2. Main sink processes

Atmospheric carboxylic acids have diverse reaction possibilities, depending on the functional groups they are provided with. While photolysis of acetic and formic acid does not occur to any significant extent in the troposphere (Calvert and Pitts, 1996), that is the principal loss mechanism of the acids with an oxo function, as pyruvic acid. Likewise, carboxylic acids with a double C-C link have short lifetimes due to their reactivity with HO radicals. The lifetimes of such reactive acids extends to a few minutes or hours at most.

Stable organic acids with low vapor pressures, as oxalic, malonic and succinic acids, associate to particulate matter, and therefore their lifetimes are related to the aerosol they condense on.

Formic and acetic acids are apparently the most abundant overall, as well as very stable in the troposphere; their HO initiated oxidation reactions possibly represent the major sink process only above the mixing layer. The lifetimes regarding HO initiated oxidation are in the order of 50 days for these acids. In the lower troposphere, dry and wet deposition significantly reduce the lifetimes of these organic acids to between one and less than ten days, with wet deposition having a potentially large contribution (*e.g.* Andreae *et al.*, 1988a; Talbot *et al.*, 1990). Unfortunately, few studies include the estimation of dry deposition rates of organic acids, and not one was found dedicated exclusively to the matter. Two studies with estimations of dry deposition rates (Helas *et al.*, 1992; Hartmann *et al.*, 1991) have led to deposition velocity estimates near 1 cm s⁻¹ for acetic and formic acids.

I.3. Basics of the daily dynamics of the boundary layer.

It is relevant for this work to explain the basic aspects of the dynamics of the boundary layer (BL). The BL is the part of the troposphere that is in close contact to the surface of the ground or of water bodies. It responds to the underlying surface's forcings - frictional drag, evapo-transpiration, heat and mass transfer, flow modifications by the terrain, etc.with a timescale of ca. 1 hour or less. In the BL, wind blows at subgeostrophic speeds, is affected by orography and convection, and usually does not follow the geostrophic direction. The BL can be several meters to several km thick. In the BL, transport of heat, momentum, water vapor and other chemical species is dominated by turbulence. In the lower 10% of the BL, turbulent fluxes and stress vary in less than 10% (Stull, 1992); this part of the BL is called the surface layer. In the layer a few mm to cm thick over each surface (the interfacial layer), transport of chemical species is dominated by molecular diffusion. The BL is usually turbulent and throughout well mixed, but at night, the less turbulent, stable, nocturnal boundary layer (NBL) forms adjacent to the cooling ground surface. Immediately above the NBL remains a well mixed, neutrally stable - not stratified - layer often called the fossil or residual layer (RL). While horizontal transport - advection - in the BL is dominated by the mean wind direction, vertical transport is dominated by turbulence. Above the BL is the free troposphere (FT), which is stratified and presents winds with geostrophic speed and direction (Oke, 1992; Garratt, 1992; Stull, 1992).

The dynamics of the BL are influenced by factors as advection and the temperatures of the ground or water surface and of the air itself. Turbulence in the BL can be caused by wind

shear at the top of the ML, by thermal convection, or it may be induced by surface irregularities. In tropical environments as those involved in this work, thermal convection is by far the most important cause of turbulence in the BL.

Figure I-1 schematizes the daily cycle of the BL under clear sky conditions at a continental location. Under such conditions, at dawn, the NBL has reached a thickness of 100 to 400 m. Once the ground is warmer than the air above it, due to solar warming, thermal convection sets in, and a mixing layer (ML) starts to develop. The relatively shallow NBL is quickly incorporated into this mixing layer –it is *entrained*. The inversion capping the NBL disappears into the ML and above it follows the air of the RL. Entrainment of the RL into the ML incorporates horizontal momentum, and the wind starts picking up near the ground. The energy needed for entrainment is provided by the warm ground surface; it occurs by means of *thermals*.





clear sky (after Garratt, 1992). A marks the starting development of the day's mixing layer, followed by the breakdown of the NBL; B marks the starting development of the surface inversion which caps the NBL, and decouples the previous ML from the ground, turning it into a neutral (not stratified) residual mixed layer.

A thermal is a rising column of warm air that is buoyant; the horizontal scale of a thermal, including the corresponding downdraft around it, is in the order of 1.5 times the thickness of the ML; their vertical extent is *ca*. the ML thickness (traditionally named Z_i , after the capping inversion). At the top of a thermal, entrainment occurs, while between thermals there is subsidence. Updraft velocity in a thermal is typically in the order of 1 or 2 ms^{-1} and can exceptionally reach more than 5 ms⁻¹; the vertical circulation period of the air in the ML -from the surface to the top of the ML- is usually in the order of 5 to 15 minutes, and during the afternoon it is in the order of 10 to 20 minutes (Stull, 1992). Entrainment of the RL is little energy consuming, because the RL is not stratified, but neutrally stable. For this reason, on clear days, the entrainment zone (EZ) may easily reach the free troposphere (FT) before or near midday. The slower entrainment of the stratified FT air continues to thicken the ML until around 13:00 or 14:00 LST, after which changes in Z_i amount to less than 10% for the rest of the afternoon. Because entrainment occurs essentially by means of thermals, the thickness of the EZ is in the order of ca. 0.4 Z_i , with Z_i defined as the local average height at the top of the EZ. Hence point measurements of Z_i – typically made with sondes – have a rather large uncertainty (ca. 40%), and use of aircraft to obtain an average estimate of Z_i over the area gives more reliable results (Stull, 1992).

In a convective mixing layer (CML) in a tropical environment, variables such as wind, temperature and concentrations of gases and aerosols are essentially constant above the surface layer. Within the surface layer, species with sources or sinks at the surface show concentration gradients that are steepest in the few centimeters next to it. On normal day in a treeless flat landscape, most of the concentration gradient occurs in the first 3 to 5 meters above the ground surface. Measurements made above about 4 m differ from the average ML value in less than 10%. During the morning hours, intensive entrainment of air from a layer that may have very different properties from those of the developing ML, has an important influence. The afternoon hours, during which the ML is in a *quasi* equilibrium because Z_i remains essentially constant at its maximum and there is a short circulation period (Stull, 1992), are of particular value for ground based observations because of the representativity of the data.

Cooling of the ground occurs in the late afternoon and night, as soon as the solar heating rate is slower than the cooling rate; usually, the most important mode is radiative cooling.

Radiative cooling is faster and more significant under a clear sky. The NBL, a stable layer of colder, less turbulent air, develops over the cooling ground throughout the night. This layer is decoupled from the remaining mixed layer above it, the RL, and is capped by an inversion. Though localized disturbances of the NBL due to shear at its top occur during the night, it is a stable layer. The NBL continues to deepen throughout the night; NBL depth increase with the square root of time has been observed by several workers (Stull, 1992). In the tropics, depths of the NBL at dawn can often be between 100 and 400 m (Martin *et al.*, 1988; Nobre *et al.*,1997; Amman,C., personal communication, 1999). A nocturnal low level jet (up to 30 ms⁻¹) frequently develops during the night just above the capping inversion, in the lower part of the RL, often with supergeostrophic wind speeds; this jet can be hundreds of kilometers wide and a thousand in length (Stull, 1992). In lowland tropical environments, there is usually little or no breeze and almost no turbulence in the NBL; most of the turbulence in the tropical lowland NBL derives from waves and shear induced by the wind in the RL (Stull, 1992).

In contrast to that occurring in a ML, emissions originating within a stable BL, as the NBL, extend within it in layers a few centimeters to meters thick – depending on the amount of turbulence – so that very high concentrations of the emitted species can be found at considerable distances from the source. Therefore, measurements of species with local sources within the NBL should be expected to yield the most variable and least representative data during the daily cycle.

For further information on the dynamics of the boundary layer, the reader is referred to specialized texts as those of Stull (1992), Garratt (1992) and Oke (1992).

I.4. Scope of this work

This study contains the results of two field campaigns that were carried out in tropical rainforest areas. The locations and season were chosen so as to have incoming wind (Trades) from above the ocean, in order to ensure a continuous renewal of "pristine" air coming from the marine boundary layer. This air should gradually become more and more concentrated in the species that characterize forested areas, among them organic acids. That should hypothetically result in concentration gradients with distance from the coast, which in turn should be observable in rainwater as well as in the gas phase.

The first of these field works was carried out in Costa Rica, in July 1996, that is, during the rainy season. There, rainwater was collected at several sites at different distances from the coastline. Organic acids and other species in the rainwater samples were analyzed. Parallel ozone measurements were made at an intermediate site. The second field work was carried out in the general framework of the LBA-CLAIRE campaign in Surinam, in March 1998, towards the end of the local short dry season. Gas phase organic acids were sampled at an inland site, about 550 km downwind from the coast along the average wind direction. Additional data of ozone and CO concentrations were obtained at the inland site and at a coastal site.

The main goal was to observe expected compositional gradients with distance from the coast, especially those involving organic acids, and interpret them. Additional measurements were made to support interpretation of the results.

II Experimental Part

The experimental work is described in this chapter in three categories: chemical analysis (section 1), sampling work and meteorological measurements (sections 2 and 3).

II.1. Chemical Analysis

All species analyzed in the laboratory for this work were ionic in aqueous solution. Ion chromatography and capillary zone electrophoresis were both employed. The list of measured species is shown in Table II-1, together with the limit of detection (LOD) estimated for them with each method. The description of the calculations for uncertainty and LOD can be found at the end of this section.

method/ species	HPIC	CZE	method/ species	HPIC	IEC	CZE
Na⁺	0.23	NA	acetate	0.31	0.63	0.39
K⁺	0.12	NA	formate	0.37	0.42	0.85
NH_4^+	0.14	NA	lactate	0.43	0.48	0.35
Mg ²⁺	0.08	NA	oxalate	0.1	NA	0.68
Ca ²⁺	0.15	NA	propionate	0.16	0.24	NA
CI⁻	0.42	2.6	pyruvate	0.16	NA	NA
NO_3^-	0.4	0.72				
SO ₄ ²⁻	0.38	0.67	phosphate	0.52	NA	0.40

Table II-1. Ion species analyzed and limits of detection (µM) with employed methods

NA = not analyzed. **HPIC** = ion exchange chromatography. **IEC** = ion exclusion chromatography. **CZE** = capillary zone electrophoresis.

II.1.1. Materials

All water used had been freshly deionized by means of a Milli-Q battery (Millipore, Bedford, Massachusetts, USA) and had a conductance lower than 8 μ S. All substances used for preparation of standard solutions were perfectly dry; purity was 99 % or higher, except in the case of sodium lactate (Aldrich), which had >96% purity. Materials and reagents used experimental

for specific purposes (specific analysis methods, sample collection, preservation, etc.) are described in later sections of this chapter.

II.1.2. Ion Chromatography (IC)

Ion chromatography was the major analysis method employed in this work. Table II-2 summarizes the main characteristics of the instruments and methods used. Further details regarding the methods are given in subsequent sections.

	AEC	IC anions	IC cations
Eluent	1 mM perfluorobutyric acid / isocratic	NaOH 0.2 to 30 mM / gradient; degassed	MSA 10 mM / isocratic; degassed
Sample loop	PTFE 50 µL	PTFE 100 µL	PTFE 100 µL
Sample injection	manual	Milton Roy LC 241 autoinjector	Milton Roy LC 241 autoinjector
Separator Column / Column Guard (capacity)	Dionex HPICE AS1 (27 µeq)	Dionex AS-11 / AG-11 (45+ 9 µeq)	Dionex CS-14 / CG-14 (1,3+ 0.26 µeq)
Col. temperature	37 °C	room	room
Pump	Sykam S3110	Dionex GPM-2	Shimadzu LC-9A
Flow	0.7 mL min ⁻¹	1 mL min ⁻¹	1 mL min ⁻¹
Conductivity suppression	Dionex AMMS-ICE Regenerant: TBAOH 8 mM at 2 mL min ⁻¹	Dionex ASRS-I and - ultra; electrochemical mode	Dionex CSRS-I ; electrochemical mode
Detector	Sykam S-3110	Made at the MPI	Dionex CDM-1
Run duration	20 min	26 min	10 min
Recording	PC with ELAB [™] chromatography system (OMS Tech., Miami)	PC with ELAB [™] chromatography system (OMS Tech., Miami)	PC with ELAB [™] chromatography system (OMS Tech., Miami)

Table II-2. Ion chromatographic setups used in this work

TBAOH = tetrabutylammonium hydroxide; MSA = methanesulfonic acid

Integration of the chromatograms was achieved by use of the ELAB[™] software or of the P-Surf software (written by F. Helleis, MPI , Air Chemistry Department).

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II.1.2.1. Anion Exclusion Chromatography (AEC)

The principles of separation in anion exclusion chromatography are: a) Donnan exclusion, b) Steric exclusion and c) Polar and van der Waal interactions. The stationary phase is a totally sulfonated cation exchange resin (the resin of the AS-1 column, used here, is totally sulfonated polysterene/divinylbenzene).; the mobile phase is slightly acidic water (ca. 1 mM in a strong monoacidic acid, as octanesulfonic or perfluorobutyric). The Donnan membrane, consisting of layers of water molecules attracted by the negatively charged sulfonate functions of the membrane, repels the anions due to their charge. Neutrally charged molecules penetrate, however, the Donnan membrane. They thereby interact with the resin and are subject to the effects of steric exclusion and adsorptive forces. Partition of alcohols, sugars and other polar but neutral substances is thereby obtained. In the case of weak acids, an additional factor gives the Donnan exclusion an important role in their separation. Because weak acid molecules are ionized part of the time, they are excluded part of the time from the Donnan membrane, and part of the time they can penetrate it. Their dissociation constant (k_a) determines their retention time to a greater extent than the other effects occurring once the molecule penetrates the Donnan membrane. In this way, weaker acids have longer T_R , and strong acids are not retained at all (Gjerde and Fritz, 1987).

After separation of the organic acids, the suppression of acidity by use of a Hydroniumpermeable membrane situated after the column allowed the weak acids to dissociate and be detected by conductivity, while it also lowered the background signal.

AEC was employed to determine the contents of HCOOH, CH₃COOH and CH₃CH₂COOH in the rainwater samples collected in Costa Rica, in 1996 (chapter IV). Similar methods have been described by Elbert *et al.* (1989) and Cheam (1992) previously. As eluent, a 1 mM solution of heptafluorobutyric acid (Aldrich; 99%) was used (as recommended in the manual for the Dionex HPICE-AS1 column), instead of the 1 mM HCl or Octanesulfonic acid often used previously for the same and equivalent separator columns.

Figure II-1 shows chromatograms of standards and one rainwater sample collected in Costa Rica about 50 km inland from the coast. The water dip occurred 7.5 minutes after injection

and was used as time zero. Separation of the more frequently seen organic acids therefore took somewhat more than 16 minutes. As seen in the sample chromatogram, aditional peaks appear between the water dip and the formic acid peak. The first small peak immediately after the water dip was an artifact and did not appear each time when injecting the same sample. The second peak corresponds to a group of unidentified anions in the samples eluting with a similar retention time (T_R) as lactic acid. In order to quantify these in some way, lactic acid was included in the standards. This group of anions (hereafter LAC-group) eluted in a single peak sometimes with one or two shoulders. As it could be later shown, the LAC-group can be attributed to the bottles (of fluorinated HDPE) used for sample collection. This is explained in more detail in the section of this chapter about sample collection.



Figure II-1. Anion exclusion chromatograms of standards and one sample. Conditions used are in Table II-2

Inorganic anions were not analyzed by this method, since they were not retained by the column, but by capillary zone electrophoresis (see ahead in this chapter).

II.1.2.2. Ion Exchange Chromatography (IEC)

IEC was used in this work to analyze cations and anions. The principle of separation is differing retention of the solute ions in the column due to their differing electrostatic and polar interactions with the stationary phase (Gjerde and Fritz, 1987). Suppression was employed to reduce the OH^- (anions analysis) or H_3O^+ (cations analysis) concentration in the mobile phase, thereby reducing background conductivity.

The major cations $(Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+})$ in rainwater samples were separated isocratically with an acidic mobile phase. The method and instrumentation were fast and simple, especially compared to those employed for analysis of anions. Figure II-2 shows chromatograms of standard solutions and of a sample collected at the coast. Table II-2 contains other relevant details about the analysis method.



Figure II-2. Cation exchange chromatograms of standards and one sample. Conditions used are in Table II-2

The vials used to keep samples and standards, made of polypropylene, were tested for adsorption of cations on their walls. Results showed that measurable adsorption of the analyzed cations did not take place. Two different tests were carried out. Vials which had held sample solution for over a year were extracted for 10 hours with 1 mL of a 100 mM HNO₃ or MSA solution; the extract was then analyzed for cations. The same was done with vials which had contained standard solutions with concentrations of up to 500 μ M of the cations for over 5 days. In this way it was proven that neither time nor concentration of the vials.

Inorganic and organic anions were analyzed by exchange chromatography on the same column (Dionex AS11) in a single run. Retention times of more highly charged anions, as well as of anions of strong acids, were longer than those of the anions of weak organic acids. Intentional and perfectly reproducible gradual variation of the composition of the mobile phase, in order to change the retentivity of the stationary phase, is known as the use of a gradient, and refers to the variation in the mobile phase composition in time. The use of a gradient with the AS-11 allowed for good resolution of most anions of interest. The resolution of the peaks was good at T_R larger than that of acetic acid. But resolving acetate from lactate satisfactorily became a major issue, because one or more peaks could show up in the samples around the T_R of lactate, similarly to that seen with AEC (see previous section), and acetate was present in all samples. Several gradients were developed to resolve fast eluting anions better than the gradient recommended in the column manual (Dionex AS-11 column manual), without extending the length of the run by more than 5 minutes.

The set of conditions characterizing the best gradient is in Table II-3. It achieved better resolution and shape of the first two peaks, but only about 30% of the samples from Surinam could be analyzed with it. The nominal concentration of the standards corresponds approximately to that of most anions, with the exception of propionate, pyruvate, and oxalate, which were 1/3, 1/2 and 1/4 times as concentrated, respectively. These concentrations were used in approximate accordance to the proportions of the different anions in real samples. The most diluted standard used was nominal 0.5 μ M, while the most concentrated was usually nominal 25 μ M.

time / min NaOH / mM		flow /mL min ⁻¹	time / min	NaOH / mM	flow /mL min ^{−1}
0.5	0.15	1	15.5	24	1
2	0.4	1	16	25	1
3	0.55	1	18	40	1
6	0.75	1	19.5	35	1
8	2.5	1	23	0	1.5
9.5	5	1	24	0.15	1.5
14	10	1	25	0.15	1
14.5	15	1	28	0.15	1

Table II-3. Gradient used for separation of anions with LBA-CLAIRE samples.

Time listed is when the given conditions were reached. Conditions varied linearly in time. The time frame of a single analysis was 28 minutes.

In Figure II-3, chromatograms of standards are shown above one of a sample collected in Sipaliwini, Surinam, during the LBA-CLAIRE campaign. The chromatograms shown in Figure II-3 were obtained with an earlier gradient; better resolution and shape of the first two peaks was achieved with the last gradient, in Table II-3.

As seen in the figure, lactate was also in the present case one of the fast eluting anions. Samples showed a multiple peak with a similar retention time (T_R) to that of lactate also in the present case; it will also be named LAC-group here. Several organic anions were found to have a T_R that was comparable or even coincident with that of lactate, both with AEC and with IEC; several of them may have been present in the LAC-group appearing in the chromatograms of the samples. Some of them are 3-hydroxypropionate, 3hydroxybutyrate, 2-hydroxy-2-methylpropionate and succinate. The T_R of lactate was used as the reference for the multiple peak because it could not be further resolved; the resolution of acetate from lactate was already a major achievement.



 Figure II-3. Anion exchange chromatograms of standards and one sample. Peaks correspond to:
 1- LAC-group , 2- acetate, 3-propionate, 4- formate, 5- pyruvate, 6- chloride, 7- nitrate, 8carbonate, 9- sulfate, 10- oxalate, 11- artifact, 12- phosphate. See comments in text.

II.1.3. Capillary Zone Electrophoresis (CZE)

CZE basically employs a capillary filled with an electrolyte solution and a high voltage source, used to apply usually 10 to 30 kV across the length of the capillary. The sample is introduced at one end of the capillary and the detector is placed near the other end. Application of the voltage causes electrophoretic and electro-endo-osmotic movements which result in the migration of the capillary (*e.g.* Altria, 1996; Engelhardt *et al.*, 1994). Separation occurs due to the differing mobilities of the ionic species; mobility is mainly determined by charge and size of the ionic species; the separated species travel in "zones" towards the other end of the capillary (from here the name of the method), where the detector is. Indirect UV is a very common type of detection used in CZE; that was the type of detection used in this work. For indirect UV detection, a strongly absorbing ionic species

is put in the electrolyte (in the present case it was CrO_4^{2-}), and the wavelength absorbed by the species is selected in the detector. The light crossing the capillary is strongly absorbed by this species. The detector is set in the absorbance mode; and registers this strong absorption. The migrating sample ions displace a charge-equivalent amount of electrolyte ions in the zone they are grouped in. This zone passes through the part of the capillary where the detector is operating. Because the analyzed ions do not absorb in the same wavelength as the electrolyte ions, a weaker absorption is registered for an instant. This leads to a negative peak in the absorbance, whose size is proportional to the concentration of the species causing it. The signal is inverted, in order to have positive peaks and integrate them with standard chromatographical software.

CZE was employed in this work to quantify the inorganic anions (Cl⁻, NO₃⁻, SO₄²⁻, HPO₄²⁻) and oxalate in the rainwater samples from Costa Rica, which could not be quantified with the anion exclusion method available at that time. The setup was constructed by W. Elbert, from the Biogeochemistry Department of the MPI.

The conditions used were an optimized version of those recommended by Birgit Tenberken, from the <u>Technische Hochschule</u> of Darmstadt (personal communication, 1996). The method was modified to be able to also quantify some of the organic anions, among them formate, acetate and lactate. Samples which had not been quantified with the ion exclusion method, or whose results seemed inconsistent, were analyzed for organic anions by CZE. The optimized analysis conditions were:

Capillary: 100 µm ID; detection at 70 cm, 75 cm long.

Electrolyte: 3 mM Na₂CrO₄; 0.4 mM TTAH^{*}; 35 μ L Ca(OH)₂ saturated solution in 35 mL electrolyte.

Potential: 25 kV

^{*} **TTAH** is tetradecyltrimethylammonium hydroxide. It was obtained by eluting a 5 mM aqueous solution of the bromide (Aldrich, >99%) through a column filled with Amberlite IRA/904 (Aldrich), which is a strongly basic ion exchange resin.

Detection: Indirect UV; 254 nm.

Run: 4 to 5.5 minutes, depending on the anions of interest and on the day's performance.

Integration of the electropherograms was achieved by use of the ELABTM software or of the P-Surf software (written by F. Helleis, MPI).

The separation of the inorganic (C Γ , NO₃⁻, SO₄²⁻, HPO₄²⁻) and the organic anions (oxalate, formate, acetate and lactate) was achieved in a runtime of 5 minutes. Figure II-4 and Figure II-5 show example electropherograms of a standard and a sample. As seen there, migration time (**T**_M) and resolution of the peaks are better than in most HPLC applications. However, noise is comparatively higher, due to the very short pathlength which is available for the indirect UV-detection of the ions (100 µm in the present case) and the small amount of sample used (in the order of 100 nL).

Variability of the calibration curves from day to day was high, so that calibrations of consecutive days were rarely similar enough to be able to pool them – in contrast to the chromatographical methods. For this reason, on most occasions, only the day's standard runs were used for calibration.



Figure II-4. Electropherogram of a 5 µM anion standard. See comments in text.



Figure II-5. Electropherogram of a rainwater sample. See comments in text.

Additionally, T_M varied from day to day and also slightly within the same day, depending on the system's performance (which in turn depended on the internal surface of the capillary); the electropherograms in Figure II-4 and Figure II-5 are from different weeks and show a clear differentiation of the T_M . Standards were analyzed periodically between samples during the analysis days; in this way, any significant changes in the performance of the instrument could be immediately detected.

II.1.4. Calibrations, their uncertainty, and limits of detection.

For all ion chromatographic methods used and for CZE, calibrations were made from analyses of standard solutions by means of linear regression. Standard solutions were prepared in such a way that uncertainty regarding their concentration remained below 2%, except in the case of lactate, where the purity of the lithium salt was only >96% (Merck, Darmstadt). From the calibration curves, the concentration of a given sample was calculated from the magnitude of the signal, according to the equation

$$y = a + bx$$
,

where y is the signal and x is the concentration. The uncertainty corresponding to the calibration was obtained from the expression

where *t* is Student's at a 95% confidence level; it multiplies the estimation of the standard deviation of x_0 , which is the value of the concentration obtained (by interpolation on the calibration curve) for a sample giving a signal of magnitude y_0 . The following approximation was used, as recommended by Miller and Miller (1993), to estimate the value of the standard deviation of x_0 :

$$\mathbf{S}_{\mathbf{x}_{o}} = \frac{\mathbf{S}_{\mathbf{y}|\mathbf{x}}}{b} \left\{ \frac{1}{n} + \frac{1}{m} + \frac{(\overline{\mathbf{y}} - \mathbf{y}_{o})^{2}}{\sum_{i}(\overline{\mathbf{x}} - \mathbf{x}_{i})^{2}} \right\}^{1/2}$$

where *n* is the number of repetitions, *m* is the number of standards used, y_0 is the magnitude of the signal for the sample of interest and $s_{y/x}$ is the statistic

$$s_{y/x} = \left\{ \frac{\sum_{i} (y_{i} - y_{i})^{2}}{n-2} \right\}^{1/2}$$

with the y_i values being interpolated from the calibration curve constructed from the standard concentrations and their signal and the y_i the actual signal. The value of $s_{y/x}$ is estimated as if constant for the intervals of values of the signal from which it is obtained.

In all calibration datasets used in this work, the standard deviation of the y_i (signal) values for a chosen standard concentration increased approximately linearly with the concentration, that is, the corresponding x value. That suggested that a relative uncertainty might better represent the real uncertainty of the measurements. In order to assess this, a calibration curve, here named C_T , was constructed from the whole calibration dataset. For each standard concentration k, the uncertainty of the corresponding x_0 value, with $x_0 = k$, was calculated using the subset of standard data corresponding to $k_i \leq k$ in the expressions above. The values of y_i were therefore calculated using C_T . An example plot of these uncertainties for the chloride, nitrate and formate ions is shown in Figure II-6. As seen there, the uncertainty for the lower x_0 values holds essentially constant while that of higher x_0 values increases linearly with x_0 .

There was a linear relation of the magnitude of the uncertainty to the concentration of the analyzed sample, but the intercept was not zero. Uncertainties of the estimate of x_0 in the range of concentrations where the uncertainty increased linearly, were calculated by means of a linear equation.





For the lower range of concentrations in which the estimate of the uncertainty of x_0 was essentially constant, a new calibration curve was constructed with only the standards in that range. The uncertainty of the estimates of x_0 in that range was set as equal to that for the highest standard (x_s) concentration in the range, which holds true within 5% of the
uncertainty estimate. An example of the uncertainty estimates for this range is shown on Table II-4, where the informations relative to the estimation of uncertainty for the concentration range from 0 to 15 μ M are displayed. The group of standard data used in this example (Jul-II) comes from 5 analysis days during July 1998. The data subset is that of chloride. The concentrations of the standards are used as example concentrations for which the uncertainty of the calibration is given, on the right side of the table.

Analyte: Cl [−]	Group: JUL-II	Standard Concentration / μΜ	Uncertainty / µM
N =	22 data	0.25	0.38
up to:	15 µM	1.00	0.37
Slope (<i>b</i>)=	3850548	2.50	0.37
Intercept (a) =	247033	5.00	0.37
Correlation (R) =	0.9996	7.50	0.37
S _{y/x} =	663375	15.0	0.40

Table II-4. Data relative to the calculation of uncertainty of a calibration in the constantuncertainty range of concentrations.

Limits of detection (LOD) were determined for each analyte by multiplying by three the standard deviation of the signal value (free of outliers) obtained from all measurements of the smallest standard solution (in all cases more than 25 data), then dividing it by the average slope of the calibration curves. That is, the standard deviation of the blanks, customarily used for this purpose (Miller and Miller, 1993), was substituted by that of the smallest standard. In analysis methods like chromatography and CZE, peaks at a T_R may well appear which are below the LOD of the corresponding analyte. However distinct they may be, these peaks are customarily ignored.

II.1.5. Measurement of acidity

Measurement of pH with an electrode is the most common way of assessing the acidity of rainwater samples. Even though there are important objections to the reliability of the

method for very diluted samples, the use of an electrode is much simpler than other possibilities. In this work, pH was also measured with an electrode. An especially fast one that could yield reliable results with rainwater samples within less than one or two minutes was found and tested with very dilute solutions prepared from deionized water. A sampler cell (Figure II-7) was built around its tip in order to avoid any risk of affecting the permeable glass surface or moving the electrode. That additionally reduced the sample volume needed and its contact to ambient air. Sample and rinse solutions were sucked into the cell and expelled from it by use of a connected syringe. The response of the electrode was tested by measuring a solution (a diluted sample of rainwater) several times consecutively, without rinsing with deionized water in between, disposing each time the measured portion. The reading was constant.

The needle leading to the cell's body was PTFE tubing, the cell body was HDPE. The cell and electrode were rinsed once with deionized water and once with the sample, before filling it to measure the sample's pH.



Figure II-7. Sampler cell used for pH measurement. See comments in text.

With the sampler cell used, one measurement required 0.6 to 0.7 mL sample. The electrode had a fast response, having been designed for measurements in pure water samples. The reading was allowed to stabilize until it varied less than 0.02 pH units in 30 seconds. Each measurement took between 1 and 3 minutes. Precision of the setup and method used was tested by measuring the pH of a rainwater sample 25 times. The standard deviation obtained in this way amounted to 0.04 pH units.

The following parts were employed to measure pH in rainwater samples from Costa Rica:

Electrode: Ross 8103

pH meter: WTW pH537

sampler cell, constructed in the laboratory, at the MPI

II.2. Sampling setups and procedures

II.2.1. Rainwater sampling

II.2.1.1. Materials

An important requisite for proper sample collection and conservation is making good choice of the materials with which the samples will come into contact and the vessels in which the samples are to be kept until they can be analyzed, so that they are not a source of contamination and do not contribute to analyte loss. Surfaces coming in contact with the rainwater sampled in this work were either PTFE, polypropylene, HDPE or fluorinated HDPE. They were cleaned prior to use with methanol (Lichrosolv, Merck, Darmstadt), rinsed with deionized water, and thereafter handled with gloves. They were also isolated from ambient air when not in use. If something happened that could lead to contamination of these surfaces (a bird, a leaf, an insect, wind blowing them over, etc.), they were cleaned again in the same way.

In all cases, rainwater ended up in a collection bottle (polypropylene or fluorinated HDPE), from where it was transferred to vials (polypropylene), which were stored until analysis. New rinsed bottles and vials were tested by rinsing again for 5 minutes with 5 to 10 mL deionized water in the bottles and 1 mL in the vials (with 5 mL capacity). The rinse water was then analyzed by anion chromatography and no contamination was detected. This test was done on 5 bottles and 10 vials. The test was repeated, rinsing the same number of vessels consecutively (one after another) with a single portion of water; it lead to the same results. In this way, contamination of the samples by the materials used to collect them was hoped to be avoided.

A previous test on the vials, consisting of rinsing 10 of them (only capped, unrinsed new vials) consecutively with the same 1 mL deionized water and analyzing it for anions, had revealed several contaminants in the order or 1 to 10 μ M in this mL rinsewater. It was not certain whether the contaminants had come from one single or all of the vials, so another test on 10 individual vials was made. Several of them were only lightly contaminated, but to a variable extent. For this reason, it was decided to thoroughly rinse with deionized

water all vials and bottles which should come into contact with the samples, one last time just before use.

Nalgene[®] FLPE[®] (fluorinated HDPE) bottles were used in this work for sample collection. FLPE was the material of preference for the collection bottles due to the film of fluoropolymer that covers the HDPE, which should make it yet more inert and impermeable than plain HDPE. However, a contamination of the samples which was due to the material of the collection bottles was later discovered. Small amounts of moisture, remaining in the bottles after rinsing them, were capable of extracting several substances from the walls after some hours. Such an extract was analyzed (by ion chromatography), and several peaks were found in the chromatogram. One of these peaks, by far the largest one by a factor of 30-100, had approximately the same T_R as lactate and its 3-hydroxy isomer. The other peaks were very small and did not coincide with those of any of the analytes usually found in the samples. Therefore, substances in the samples eluting with a T_R similar to that of lactate cannot be distinguished from the main contaminant coming from the bottles. For this reason, the peaks in the chromatograms of the samples appearing where that or lactate appears have not been discussed in this work.

II.2.1.2. Rainwater sampling apparata

All-stainless-steel boxes were constructed for rainwater sampling in Costa Rica (1996). The boxes held a polypropylene funnel over a clean collection bottle. The funnel was covered by a stainless steel hood, whose upper surface was slanted towards the back of the box. The box had a lash on its back, where the hood was put after uncovering the funnel to collect sample. In this way, rainwater dripping from the hood when it was retired could not fall into the funnel. Therefore, the hood protected the funnel from dry deposition while it was not raining. And the box protected the collected rainwater from radiation and isolated it from surrounding ambient air during sample collection.

During the LBA-CLAIRE campaign Surinam, two automatic only-wet rainwater samplers constructed at the Meteorological Institute of the Stockholm University, were deployed at an inland site named Sipaliwini and at a coastal site named Alliance. The samplers had a rotatory plate with 12 sampler bottles, so that rainwater from any period could be collected in 12 different fractions. The rotation of the plate responded to a signal that could be given

by a clock or by a computer. A controller unit (built at the Electronics Department of the MPI) that could make the sampler change the collection bottle according to programmed sequence within a single rain event, was connected to the sampler. In order to avoid contamination of the rotatory plates, solenoid valves were built in to close the sample flow while the new collection bottle was set into sampling position. All parts coming into contact with the sample were HDPE, PTFE or polypropylene. The outer structure of the sampler body was PVC. The MISU samplers have been previously tested for several years in the field (L. Granat, personal communication, 1997), and have so far proven to be extremely reliable.

Because the controller unit (as explained regarding the meteorological setups) did not function properly, single rain events could not be sampled in several fractions. So they were collected each in a single bottle. As explained in the results and discussion, rainfall was anyway very scanty in Surinam during the LBA-CLAIRE campaign.

II.2.1.3. Rainwater sampling procedure.

In Costa Rica, simultaneous sampling at all sites was achieved by hiring students and assigning them to the different collection sites, where they camped for the sampling period. The students were instructed how to collect the samples at the site and how to avoid their contamination. Simple but important measures, like personal cleanliness, not eating or staying near the sampling apparatus, placing the sample apparatus as far as possible from the camp, keeping rotting vegetal material away from the sampling apparatus, sampling at least 10 meters away from the next tree, etc., were observed at all sampling sites. The sampling funnel, bottles (and tubing in Surinam), with which the sample should come into contact during collection, were rinsed with deionized water and shaken dry at the end of each rain event and every evening. All sampling implements were handled with utmost care in order to avoid any possibility of contamination. As part of the measures to ensure proper care during sample collection, a glove material was chosen (vinyl), which tore when pulling the gloves off the hands; in this way single use of gloves was ensured at all the sites. The sampling setup was kept covered when it did not rain.

In Costa Rica, once rainwater fell into the collection bottle, it was was quickly transferred to the vials. In Surinam, the sample remained in the bottles less than 1 hour at daytime and less than 3 hours in the night time.

The vials were rinsed three times thoroughly with portions of the sample, otherwise with deionized water, before filling with sample to ³/₄ of their capacity and capping. The stabilizing (details about preservation are in a section further below) substance (thymol or chloroform) was introduced immediately before capping. After capping and testing for tightness, the sample vials were marked and tightly wrapped with aluminum foil, then with Parafilm[®], marked again, then cooled or set to freeze. Unwrapped sample vials were only handled with gloves on. New vials were used only if they had their cap on in the package.

In Costa Rica, rain events were sampled in several fractions, in order to observe variation in the concentration of the analytes with the event. A first fraction was collected 10 minutes after the start of the event; further fractions were collected 30 minutes, 60 minutes, 120 minutes, 180 minutes and so forth, after the start of the event.

An event was defined as finished if rainfall ceased for 15 minutes.

II.2.2. Sampling of air moisture

In Surinam, moisture from the air was condensed in a cooled spiral (*ca.* $2 - 5^{\circ}$ C) such as that shown in Figure II-8. This sampling spiral has been used previously to collect samples for analysis of peroxides, as described by F. Sauer (doctoral Thesis, 1997), with aid of a stripping solution. The stripping solution was not necessary in Sipaliwini, due to the high absolute air humidity.

Air flow was 2.9 L/min, yielding about 0.04 mL/min condensed water. One sample was collected every 15-20 minutes. Of the water soluble gases taken up into the condensed water, hydrogen peroxide, methyl hydroperoxide, hydroxymethyl hydroperoxide (Grossmann, 1999) and organic acids were later analyzed. Further information regarding the solubility of the peroxides and their collection efficiency can be found in the doctoral thesis of F. Sauer (1997).



Figure II-8. Air moisture sampling setup, according to Sauer (1997).

II.2.2.1. Collection efficiency (CE) of the sampling coil for the organic acids.

The sampling method has been previously used, primarily to sample peroxides in air (F. Sauer, PhD. Thesis,1997). In that work, CEs for several substances were measured and compared to the values calculated from the Henry distribution coefficients (K_H). The excellent agreement (see Table II-5) found by Sauer (1997) between expected and experimental CEs shows that they can be reliably calculated for substances whose Henry distribution coefficient is known. This is shortly explained in the following lines.

The collection efficiency is higher when a substance is more soluble in water; the Henry coefficients, also shown in the table, are a solubility index, and it can be seen how the CE increases with their value.

Substance	Measured CE	Calculated CE	K _H	
hydrogen peroxide	98% ± 5%	99%	4.9*10 ⁵	
peroxyacetic acid	87% ± 5%	89%	3021	
methylhydroperoxide	77% ± 4%	76%	1100	
K _u is in mol dm ⁻³ atm ⁻¹ (O'Sullivan <i>et al.</i> 1996); values corrected for 278K by Sauer (1997)				

Table II-5. Collection efficiencies (CE) for several substances as measured and calculated by F. Sauer (Thesis, 1997).

For aqueous solutions of a gas in equilibrium with the gaseous phase, the Henry distribution coefficient is defined as

$$K_{\rm H} = C_{\rm g} \ / \ p_{\rm g}$$
 ,

where C_g is the concentration of the dissolved gas (usually in mol dm⁻³) and p_g is the partial pressure of the gas over the liquid. The CE of the sampling coil, assuming equilibrium between the sampled gas and the liquid phase is reached, can be expressed as

$$CE = \{ 1 + F_g / (F_l * R * T * K_H) \}^{-1}$$

(Sauer, 1997) where F_g is the temperature and pressure corrected gas flow , F_l is the flow of the liquid, R is the gas constant and T is the temperature. Units used here were dm³ min⁻¹ for flow, K for temperature, mol dm⁻³ atm for K_H, and 0.08206 dm⁻³ atm mol⁻¹ K⁻¹ for R.

The good agreement found by Sauer (1997) between measured and calculated (from published K_H data) collection efficiencies of several gases (Table II-5) implies that equilibrium is effectively reached in the sampling coil. Therefore, with reliable K_H data, the CE for other substances being sampled in the coil can be calculated and used. This was done for the organic acids analyzed in this work.

As defined above, K_H considers the concentration in solution of the actual substance corresponding to the gas. However, when dealing with species that reversibly associate with water or dissociate in it, the fraction of the substance reacting must be considered. A corrected K_H , called 'effective' K_H is valid for these substances. For a weak acid HA, like the organic acids sampled, $k_a = [H^+][A^-] / [HA]$, where k_a is the dissociation constant of

the acid in the aqueous phase; this implies that $[A^-] = k_a [HA] / [H^+]$, so the total concentration of the substance in the solution at equilibrium is

$$[HA] + [A^{-}] = [HA] + k_a [HA] / [H^{+}] = [HA] (1 + k_a / [H^{+}])$$

Hence the 'effective' K_H (hereafter K_{Heff}), is expressed by

$$K_{\text{Heff}} = K_{\text{H}} (1 + k_a / [\text{H}^+])$$

The major organic acids analyzed in air samples in this work were HCOOH and CH₃COOH; and the values related to the calculation of their collection efficiency are shown in Table II-6. The flow of the collection liquid was between $3.5*10^{-5}$ dm³ min⁻¹ and $5*10^{-5}$ dm³ min⁻¹. The pH values of the samples were between 4 and 5. The calculated CE values varied slightly with the pH of the samples and with the flow of the liquid in the coil, as shown in the table.

Table II-6. Parameters for the calculation of collection efficiencies for CH₃COOH and HCOOH with the sampling coil.

Substance	К _н at 298 К	К _н at 275 К	k _a	K _{Heff} at pH = 4 and 5	CE at 275 K
НСООН	5300	24 307	1.77*10 ⁻⁴	$7.4^{*}10^{4} - 5^{*}10^{5}$	97% ± 2% *
CH₃COOH	5200	27 995	1.75*10 ⁻⁵	$3.7^{*}10^{4} - 8.6^{*}10^{4}$	94% ± 3% *

efficiency is dimensionless as well as k_a ; MHP = Methylhydroperoxide; k_a = dissociation constant (Robinson and Stokes, 1970); K_H is in mol dm⁻³ atm⁻¹. * Variations due to pH and flow of liquid.

The values of the Henry coefficients (K_H) correspond to values on which several recent publications agree; they were extracted from a compilation on the world wide web (Sander, 1996, and references therein contained).

II.2.3. Sample preservation

How an aqueous sample is kept after collection is a critical issue for the validity of any analyses of its organic components (Wortham *et al.*, 1995, and references therein contained). Many organic components in such samples are susceptible to thermal, photolytic, chemical or biological degradation. Biological degradation is the more difficult to hinder, therefore it receives more attention (Herlihy *et al.*, 1987). Diverse bio-inhibitors

or biocides (also called "stabilizers") have been used, as a substitute or complement to refrigerating or freezing the samples.

In this work, chloroform was used to preserve the first samples, collected in Costa Rica, and thymol was used for those collected in Surinam.

II.2.3.1. Chloroform

In recent years, chloroform has been used preferentially to mercuric chloride for preservation of rainwater samples, in order to be able to quantify chloride. In this work, rainwater samples collected in Costa Rica were preserved with *ca*. 0.5% volume to volume chloroform. Chloroform used was Merck (Darmstadt) Lichrosolv HPLC quality. Samples were preserved with chloroform immediately at collection, then cooled between 5°C and 0°C, and finally frozen within 2 days after collection . All standards and blanks used for the analysis of these samples were preserved with chloroform in the same way.

II.2.3.2. Thymol

Thymol is a substituted phenol (5-methyl-2-isopropyl phenol) which possesses similar biocidal characteristics as phenol, but a higher melting point and much lower solubility in water. Its low water solubility (*ca.* 1g in 1000 mL water) keeps it from phenol's bothersome deliquescence, while its higher melting point (51.5°C) makes it easier to handle. It was investigated and proposed by Gillett and Ayers (1991) as an alternative to chloroform that could be put into the sampling vessel prior to the rain event, without risking its loss by evaporation. It has since won popularity as a substitute for chloroform in preserving rainwater samples. Its main advantages are the practicality of handling a solid instead of a liquid, better safety conditions compared to chloroform, and the fact that poisoning occurs already in the collection vessel.

Thymol (Aldrich, >99%, recrystallized from water/ethanol) was employed in this work during the LBA-CLAIRE campaign. Tests on the original reagent for contaminants or interference were carried out. Anion chromatography of rinsewater of the reagent showed that it was slightly contaminated with nitrate, chloride and several other anions. Results were the same if the crystals had been previously rinsed with deionized water, meaning that the contamination was not only on the surface of the crystals. The reagent was doubly recrystallyzed from ethanol and deionized water in order to avoid any risk of significant contamination. This procedure was effective in eliminating the contaminants. During the sampling period, small amounts of the purified thymol were carried to the field for use, while the rest of it was left back in safety in order to avoid the risk of its accidental contamination.

All samples during the LBA-CLAIRE campaign were preserved by adding one to three crystals of thymol (*ca.* 0.3 mm long) to the vial (3 - 4 mL), then they were cooled between 5°C and 0°C or else they were frozen. New thymol was added to the collection bottles each time they had been emptied and rinsed, so that the sampled rainwater was preserved with thymol already at the moment of collection. Air moisture was collected at *ca.* 3°C and kept for 1 to 4 hours below 4°C before preserving it with thymol and freezing it. This was done so, in order to avoid possible interference of thymol in the analyses of peroxides in these samples. Samples and standards put into the vials used for the autoinjector were also stabilized with a thymol crystal.

II.2.3.3. Refrigeration

All samples collected in this work were cooled between 5°C and 0°C as soon as possible after collection. Rainwater samples in Costa Rica were preserved and cooled immediately following collection. Rainwater collected in Surinam remained in the closed sampling bottle for 1 (daytime) to 3 (nighttime) hours, then it was transferred to vials, added thymol and frozen. Freezing was preferred, but was not immediately possible at two of the sites in Costa Rica. For this reason, some samples were cooled for up to 3 days between 5°C and 0°C before being frozen. Samples were only thawed shortly before analysis, then kept below 5°C for few minutes to hours and frozen again until the next analyses were due, in order to diminish risk of biological activity in the samples.

II.3. Other sensors and measuring devices used in the field.

II.3.1. CO and O₃ measuring devices.

Diverse electronic measuring devices were employed in the field to record ozone and carbon monoxide concentrations. The main characteristics of these instruments are contained in Table II-7.

Species:	со	CO	O ₃	O ₃
Instrument	Thermo- environmental 48s	Trace Analytical / G.C. Separation	Thermo- environmental 49s	Dasibi 1008 PC
Principle of detection	IR absorption	Reduction gas detector ⁺	UV absorption at 254 nm	UV absorption at 254 nm
Sites	Sipaliwini	Alliance	La Selva (C.R.) and Sipaliwini	Alliance
Precision / accuracy	±23 nmol mol ⁻¹ ±25 nmol mol ⁻¹	±5 nmol mol ⁻¹ ±5 nmol mol ⁻¹	$\pm 2 \text{ nmol mol}^{-1}$ $\pm 2 \text{ nmol mol}^{-1}$	±2 nmol mol ⁻¹ ±2 nmol mol ⁻¹
Data every :	12 s	15 min	La Selva: 1 min Sipaliwini: 12 s	1 min
Sampling height *	8 m	2 m	La Selva: 6 m Sipaliwini: 8 m	2 m

Table II-7. CO and O₃ measuring devices used in this work.

* above ground ⁺ HgO reduction and detection of Hg vapor by UV absorption

II.3.2. Meteorological setups

Meteorological stations were brought along to the two field experiments made for this work. In both cases, the structure was partly made at the MPI. The main goal of the design was achieving height as well as transportability. Both structures consisted mainly of a pole made of a light material (glass fiber, 6 m long in Costa Rica; aluminum telescopic, 9.5 m long in Surinam), onto which the sensors were attached by means of additional structural parts, most of them designed and made at the MPI. The poles were kept vertical by means of 3 or 4 lines attached to the ground. Verticality of the pole was guaranteed by regular

inspection of a permanently hanging lead attached to one of the booms. The rest of the structure was made in such a way that verticality of the pole guaranteed horizontality of the booms. The whole structure was less than half as heavy as the ones available at that time at the MPI, and could bring the sensors more than twice as high.

The wind sensors were at 6 m height above the ground in Costa Rica and 8 m above ground in Surinam, at least 300 m away from higher objects. In Costa Rica, the meteorological station was set up on the top of a *ca*. 10 m high bare hill; it was higher than most of the terrain and objects some 5 km around. Lightning rods were used in both cases.

The data recorder unit in Costa Rica was a CR25X Campbell data logger, which had been programmed to record data averaged over 1 minute. The Campbell data logger recorded wind velocity and direction, air and ground temperature, relative humidity and light intensity (Li-Cor pyranometer). All sensors used were standard ones purchased from Campbell (Essex).

The data recorder units used in Surinam, during the LBA-CLAIRE campaign, were designed and built at the Electronics Department of the MPI. Unfortunately, software and hardware problems in these units destroyed most of the data coming from the meteorological sensors attached to them. These units were also to control the rainwater samplers, but this was also not possible. The samplers had to be set on automatic mode, so they could only sample complete events. Fortunately, wind speed was recorded correctly because it was attached onto the only correctly functioning channel on the unit. The rain gauge was also on a counter channel, but a software problem affected the accuracy of those data.

experimental

III Ground based measurements during the Cooperative LBA Airborne Regional Experiment (CLAIRE)

In the framework of the LBA-CLAIRE campaign in Surinam in March 1998, ground based measurements of organic acids in the gas phase were carried out in Sipaliwini, (550 ± 50) km downwind from the coast, next to the Brazilian border. Complementary measurements were carried out in Sipaliwini and two other sites closer to the coast.

III.1. Description of the sites and the boundary layer in the area

This section makes a general description of the area and sites that the LBA-CLAIRE campaign involved in Surinam, with an emphasis on the Sipaliwini site. It additionally presents the data regarding the meteorological conditions of the local boundary layer (**BL**) during the campaign, before their discussion. Finally, the dynamics of the local BL are discussed in an attempt to gain a general view of meteorological aspects influencing the gas phase concentrations of ozone, CO and organic acids in Sipaliwini.

III.1.1.The sites

Ground based measurements were conducted at four locations, listed in Table III-1, during the campaign. Figure III-1 shows the sites North of the intertropical convergence zone (ITCZ). The author had to arrange the sites Sipaliwini and Alliance. Measurements were carried out by the MPI in Sipaliwini and by the IVIC (Instituto Venezolano de Investigaciones Científicas) at Alliance. At Petit Saut, measurements were carried out by the Laboratoire d'Aerologie, O.M.P., Toulouse, in a forest clearing about 400 m wide, near the Petit Saut dam on the Sinnamary river (D. Serca, personal communication, 1999). Balbina was a site North of Manaus where several groups carried out measurements; however, Balbina was located South of the ITCZ, so the data from this site can hardly be related to those obtained in Surinam, North of the ITCZ at the time.

SITE	LAT	LONG	ALTITUDE	COUNTRY	WORK	SITE FEATURES
			(m ASL)		GROOP	
Alliance	5°54'	-54°54'	2	Surinam	IVIC / MPI	Coastal site, upwind from small community
Petit Saut	4°55'	-53°10'	30	France (F. Guiana)	Toulouse	Forest clearing, near hydroelectric plant
Sipaliwini	2°02'	-56°08'	230	Surinam	MPI	Inland site, landing strip, mixed vegetation upwind from village
Balbina	-2°	-59°50'	100	Brazil	Several	Central Amazon, upwind from community

Table III-1. Measurement sites during LBA-CLAIRE.



Figure III-1. The ground sites North of the ITCZ during CLAIRE-I.

III.1.1.1. Sipaliwini: description of the site.

Sipaliwini is at the same time the name of the largest province in Surinam, of a river next to the border to Brazil, of an Amerindian village near the river, and of the station property of the Meteorological Service of Surinam (**MSS**) which is at the Northeast corner of this village. The village is home to some 50 inhabitants, members of the indigenous group named Trios. Trios are partially nomadic in their lifestyle, so that, although the village is a home usually to around 50 persons, hardly half so many could be called permanent inhabitants of the village. Their huts were all located downwind from the house where we conducted our measurements, as shown in Figure III-2, so that interference from smoke coming from cooking fires was rare, and only occurred during the mostly windless night hours.



Figure III-2. The sampling site in Sipaliwini during CLAIRE-I

Directly to the north of our station was a landing strip, where small aircraft landed 3 or 4 times during our stay. The part of the strip located upwind from the station was neither used nor maintained, and it separated our station from the forest, which covers the *ca*. 450 to 600 km up to the northern coastline of South America. In the direct neighborhood of the station in Sipaliwini were several patches of shrub land similar to the pseudo-savanna typical

to the region (determined by sandy, poor soils, in contrast to actual savannas), with mixed vegetation (grass, shrubs, small trees) adapted to the poor white-sand soils that characterize it. South and Southeast from Sipaliwini are major extensions of this type of pseudo-savanna. The shrub land near Sipaliwini is set on fire, at least partially, every year by the indigenous people, according to their traditions (personal communication from Mr. Glenn Landveld, MSS). There was clear evidence that the area directly around the landing strip in Sipaliwini had been burned many times in the past, and once a few months before our arrival.

III.1.1.2. Measurements conducted in Sipaliwini:

In three weeks in Sipaliwini, from March 6 to March 27, 1998, the following instruments were installed and operated:

- CO and ozone automatic analyzers (standard commercial instruments).

- Meteorological Station.

- Organic acids' sample recollection and analysis system (HPIC)

- Peroxides' sample collection and analysis systems (HPLC, described by Hellpointer and Gäb, (1989) and Sauer (doctoral thesis, 1997)).

- Rainwater sampler.

The methods and equipment are described in the experimental part (chapter II).

III.1.2. Meteorological conditions

The measurements in Surinam took place during the last three weeks (March 13 to 30) of the shorter one of the two yearly dry seasons in the area, which starts in January. At the time, the ITCZ was moving north from the latitude of Manaus, south of Surinam. The longer rainy season usually begins in Surinam at the end of March, and starts somewhat earlier in the south of the country. However, due to ENSO (El Niño) conditions, the ITCZ delayed its pass over Surinam about three weeks (Becker, 1998). Therefore, during the period of the study, meteorological conditions typical of the dry season prevailed in the area, characterized by trade winds entering the continent from E-NE direction, by the

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absence of large convective systems, and thus also by unusually little rainfall. A major disturbance occurred from March 25 to 28, when the convergent side of a mid to upper level trough around 250 hPa above Surinam caused strong subsidence in the region (Peters, 1998). The general wind direction remained, but the dry weather conditions were somewhat intensified during these days.

III.1.2.1. Wind in the regional scale.

The **wind direction** was determined in the whole region by the Trade winds, which blow over the continent mostly from E-NE near ground level during the months of February and March. Figure III-3 and Figure III-4 show the wind field of the region for the levels of 850 hPa and 1000 hPa on March 25 (provided by the KNMI). They are representative of the wind conditions in the region during most of the second half of March 1998. Exceptions to this occurred mainly after March 25, and especially after March 27, when wind from the East, Southeast and South at the 1000 and 850 hPa levels occurred.



GrADS: COLA/IGES

Figure III-3. Wind field for March 25 corresponding to the 850 hPa level. Made by W. Peters and M.A.F. Silva using the global model from the CPTEC. Initials in circles indicate location of the measurement sites.

Wind speed in the middle and upper boundary layer (500 to 1500 m) has been obtained from the onboard global positioning system (GPS) of two aircraft. During transport from and to Sipaliwini on March 16 and 19, on a small commercial Cessna aircraft, position and wind speed data were obtained by means of the GPS on board. The wind speed within the boundary layer (BL), about 500 m asl and above, was found to be 7.5 to 8 ms⁻¹ during these two flights. The data from the Cessna Citation jet (about the aircraft: Bregman *et al.*, 1997; Lelieveld *et al.*, 1997), from which the airborne measurements were conducted during the campaign, show wind speeds in the boundary layer in the area between 5 and 10 ms⁻¹ (B. Scheeren and J. Williams, personal communication, 1999). The wind speed vertical profile over Sipaliwini obtained from the Citation during flight 2 on March 15 (data synchronized and kindly provided by J. Williams) shows 8 ms⁻¹ for the middle and upper BL (about 500 to 1500 m asl). The wind speed data above the BL, obtained also from the aircraft, were in the order of 15 to 20 ms⁻¹.



GrADS: COLA/IGES

Figure III-4. Wind field for March 25 corresponding to the 1000 hPa level. Made by W. Peters and M.A.F. Silva using the global model from the CPTEC. Initials in circles indicate location of the measurement sites.

The prevailing conditions in the area, this is, the absence of large scale convective systems and therefore of major rain events, wind direction from E-NE, mean wind speeds in the order of 8 ms^{-1} in the BL and below 6 ms^{-1} near the ground, and mostly clear skies, will from here on be referred to as 'normal conditions'.

III.1.2.2. Meteorological conditions in Sipaliwini

Sunrise was between 06:30 and 07:00 LST; sunset was between 18:15 and 18:45 LST.

Rainfall was rare; during our stay, some 8 to 10 drizzle events and a handful short showers occurred.

Temperatures varied between around 19°C at early morning and about 27°C during the afternoon. The hottest days were the last three, with afternoon temperatures over 30°C; March 26 was the hottest afternoon, with 37°C as maximum temperature. The high temperatures coincide with the days when strong subsidence was taking place, according to Peters (1998).

Wind in Sipaliwini during the daytime normally came from NE to E, in accordance with the records from the aircraft and with the calculations made with the satellite data, already shown. Wind speed 6 m above the ground was between 2 and 6 ms⁻¹ from about 10:00 to about 17:00 LST. At night there was usually little or no wind near the ground; gusts came from E to NE, and the direction of occasional light breeze was erratic. Wind speed data for Sipaliwini from March 13 through March 27, 1998, are available. A general pattern was common to most days; the average, shown in Figure III-5, is representative of the usual conditions in Sipaliwini during the period. This average wind speed pattern was obtained from the data of 10 days having similar conditions. It excludes the wind speed data from March 22, 23 and 27 because they showed strongly untypical variation patterns; those of March 14 and 16 are not available. Hourly means from the individual days are shown in Appendix 2.



Figure III-5. Hourly wind speed means in Sipaliwini 6 m above the ground. Error bars represent 1 sd, N = 10; sensor's detection limit = 0.5 ms^{-1} . The line links the mean values >0.5 ms⁻¹.

The nocturnal values were usually under the sensor's detection limit (0.5 ms^{-1}) . However, as the standard deviations in Figure III-5 show it, there was considerable dispersion of the nocturnal hourly means, especially after 23:00 LST. This was due to occasional wind gusts occurring at night, which came from a clear northeasterly direction, as said above.

Wind speed in Sipaliwini showed a definite rise between 8:00 and 9:00 LST; before this, hourly means were generally lower than 0.5 ms⁻¹, mostly zero. Exceptions to this were March 19, 25, 26 and 27. Wind speed maxima occurred usually between 10:00 and 13:00 LST, and hourly means were usually under 4 ms⁻¹. After about 17:30 LST there was usually windstill interrupted by frequent wind gusts. A short period of complete windstill usually came after about 20:00. It was followed by windstill and occasional gusts for the rest of the night.

The last three days of our stay (25-27 March) were exceptional in that the wind picked up 2 to 4 hours earlier than usual. This coincided with the strong subsidence reported by Peters (1998) as taking place in those days.

III.1.3. The dynamics of the boundary layer in Sipaliwini

The basic description of the BL dynamics in the introduction is essentially representative of the conditions during our stay in Surinam. Based upon the data that have been presented so far, the dynamics of the boundary layer (BL) at the sites North of the ITCZ are discussed in the next subsections. Later interpretation of the data involving the chemistry of the BL is based on this discussion of the BL dynamics.

III.1.3.1. The daily cycle of the boundary layer in the Sipaliwini area.

As previously said, weather conditions in Surinam, and in particular in the Sipaliwini area, were fairly uniform during the campaign. In Sipaliwini, weather was fair and the sky was mostly clear. Few days in the Sipaliwini area were significantly different from the rest in one or more ways – rain, cloudiness, wind starting before 8:00 or before dawn, etc. Normal weather conditions included wind picking up between 8:00 and 9:00 LST and coming approximately from NE, wind speeds near the ground below 6 ms⁻¹ , mean BL wind speed in the order of 8 ms⁻¹, few clouds in the sky, temperatures between 19 and 27°C, etc. These "normal" conditions are used as the base for the discussion of data presented in following sections; in the next paragraphs is a discussion of the corresponding normal daily cycle of the BL in Sipaliwini.

In Sipaliwini, the NBL typically had little or no breeze and almost no turbulence; most of the turbulence in the NBL probably derived from waves and shear induced by the wind in the RL (Stull, 1992). As shown in Figure III-5, a definite rise in the wind speed occurred in Sipaliwini regularly between 8:00 and 9:00 LST. This seems to imply that, in the Sipaliwini area, the NBL decayed around 8:00 LST, introducing horizontal momentum from the RL, thereby causing the wind to pick up. The FT was reached by the entrainment zone (EZ) sometime in the late morning; because of the geostrophic wind in the FT, entrainment of FT air may have also contributed to maintain or raise the wind speed in the ML. A daily maximum of wind speed regularly occurred between 11:00 and 13:00 LST; afterwards wind

speed generally tended to decrease more or less linearly during the afternoon hours. Loss of horizontal momentum in the ML due to friction with the ground surface necessarily occurred as soon as the wind picked up at the surface. Entrainment of FT air, while more energy demanding, was slower than entrainment of RL air; this implies that horizontal momentum was more slowly incorporated into the ML once the EZ reached the FT; at some point horizontal momentum losses by friction became larger than the gain, and this marked the maximum wind speed for the day. Therefore, the EZ presumably reached the FT shortly before the day's wind speed maximum, which usually occurred between 11:00 and 13:00, and the ML presumably reached its maximum depth – variation under 10% – shortly after the day's wind speed maximum. The **nocturnal** boundary layer (NBL) started to develop around 17:00 - 17:30 in Sipaliwini.

III.1.3.2. Estimations of the depth of the ML and the NBL.

The depth of the ML (Z_i) can be determined experimentally by measurements of the profiles of any of several parameters. The main requirement is that these parameters be strongly influenced by the surface below (land or sea), so that the essentially homogeneous value in the mixing layer differs clearly from that of superior layers. For such parameters, the ML exhibits quite homogeneous values in its upper 90%, up to the entrainment zone. Some parameters strongly influenced by the underlying surface are temperature and the concentrations of aerosols and of several gases emitted at the surface or with large deposition velocities, *e.g.* water vapor, biogenic NMHC, ozone and CO₂.

During the LBA-CLAIRE campaign, profiles of several parameters were obtained. Continuous airborne data were recorded during 10 flights over land and /or sea, on board of the Cessna Citation experimental jet (Bregman *et al.*, 1997; Lelieveld *et al.*, 1997). Among the parameters measured were temperature, wind speed (with the GPS), pressure, particle counts, CO, CO₂, water, methanol and isoprene (Warneke, doctoral thesis, 1998; Warneke *et al.*, 2001; Pöschl *et al.*; 2001). Vertical profiles of these parameters were obtained over several representative locations in the area. Over Sipaliwini and neighboring areas, flights 2, 3 and 6 (made on March 15,17 and 22 respectively) provided vertical profiles from which the local ML depth was derived in this study. These profiles were the ones obtained nearest to Sipaliwini, and the days when

they were obtained had normal weather conditions, so the data may be considered representative for the Sipaliwini area during most of the campaign.

On March 15 (flight 2) at *ca.* 14:15 LST, vertical profiles of potential temperature (Θ), OPC (particle counts, >1µm), and CO₂ (J. Williams, personal communication) over the Sipaliwini area, lead to Z_i values of 1470 m, 1520 m and 1560 m, respectively. Water and methanol vertical profiles obtained during the same flight (Warneke, doctoral thesis, 1998) point to a Z_i value around 1480 m. Vertical profiles of Θ from flight 3 on March 17, at *ca.* 15:30 LST, over Sipaliwini and a nearby area lead to a Z_i value of about 1200 m. Vertical profiles of Θ and wind speed from flight 6 on March 22, at *ca.* 14:30 LST, over a nearby area lead to a Z_i value of about 1250 m. A *'normal'* afternoon Z_i value of 1400 ± 100 m will therefore be assumed for Sipaliwini.

Similar results have been obtained previously by other workers. During the ABLE-2A campaign, by use of vertical profiles of temperature, Martin *et al.* (1988) found the mean maximum depth of the ML to be *ca.* 1200 m; it was reached around 13:00 LST and thereafter showed only small variation (see Figure III-6).



Figure III-6. Experimental record of ML growth on an "undisturbed" day during the ABLE 2A campaign (after Martin *et al.*, 1988). Filled squares are averages of 2-3 data points lying very close together. Dash-dot lines enclose the afternoon values representing a fully developed ML.

Nobre *et al.* (1997) reported similar heights $(1200 \pm 50 \text{ m})$ for Rondonia over the Amazon forest, also obtained by means of vertical temperature profiles, that time with sondes. In both cases, the convective ML depth varied less than 10% during the rest of the afternoon. These previous data coincide well with the ML depth found for the Sipaliwini area, even though they were obtained in more continental environments, further inland.

From vertical profiles of Θ recorded above the coastal waters of Surinam, the depth of the marine boundary layer was estimated in *ca*. 600 m. This is a typical MBL depth in tropical latitues, according to Stull (1992). About 40 km inland (*ca*. 55 km downwind from the coast) Z_i was estimated in 750 m to 900 m, also from profiles of Θ , the potential temperature. This and further data are summarized in Table III-2. As it seems, the afternoon ML depth increased with distance to the coast with a nonlinear trend, like those shown in Figure III-7.



Figure III-7. Variation of the afternoon Z_i with the distance to the coast along the general wind direction. The nonlinear fits are sigmoidal (black dash-dot) and polynomic of order 2 (gray dashes), they approximately show the likely variation of Z_i with distance from the coast.

Each day during the afternoon, until the solar heating no longer provided the energy necessary to maintain the entrainment rate, the variation of the ML depth with distance from the coast may have been similar to the nonlinear fits shown in Figure III-7. Thereafter, the local Z_i at each location probably decreased somewhat during the rest of the afternoon, due to advection of the profile – of Z_i vs. distance – inland.

Table III-2. Summary of ML depths at several locations in Surinam during the LBA-CLAIRE campaign.

Location	Estimated ML depth	Parameter used
Above coastal waters	<i>ca.</i> 600 m	Temperature
55 km inland	750 - 900 m	Temperature
Sipaliwini	1400 ± 100 m	Θ , particle counts, CO ₂ , H ₂ O,methanol

At late afternoon, the NBL started to develop over the land surface. Unfortunately, neither nocturnal flights nor meteorological soundings were made during the campaign, so the depth of the nocturnal boundary layer (NBL) could not be determined and the presence of a nocturnal low level jet was not confirmed. However, other investigators have made measurements of the NBL depth in similar environments and conditions. C.A. Nobre *et al.* (1997) found the nocturnal boundary layer (NBL) above the Amazon forest in Rondonia to generally develop rapidly to about 150 m until *ca.* 20:00 LST, after which it grew slowly up to *ca.* 300 m during the rest of the night. In this light, a NBL depth of 150 to 200 m between 20:00 and 23:00 LST and a final NBL depth of around 300 m are reasonably probable estimates for Sipaliwini.

III.1.3.3. Advection of the marine boundary layer into the continent.

The general situation in the area was that the BL over the land surface – a convective mixing layer at daytime – had been advected into the continent as a marine boundary layer (MBL) from above the North Atlantic ocean. A similar situation has been described by Avery *et al.* (2001) for a coastal site in North Carolina.

At daytime, the incoming MBL was turned into a convective mixing layer over land and advected further inland at about 7 ms⁻¹; above, the free troposphere (FT) was advected inland at geostrophic speeds, closer to 15 or 20 ms⁻¹. The boundary layer deepened with distance from the coast due to the thermal convection produced by the solar heating of the land surface; as previously said, the increase rate of Z_i near the coast was estimated in *ca*. 3.60 m km⁻¹, and the depth of the fully developed ML in the Sipaliwini area – *ca*. 550 km downwind from the coast – was around 1400 m.

In the night time, once the NBL started to develop over the land surface, the newly decoupled and well mixed residual layer (RL) was advected above the NBL further inland. At the coast, the MBL was advected inland over the NBL, as a RL. A nocturnal low level jet may have developed above the NBL; in any case, the wind velocity and direction in the RL were probably nearly geostrophic, as is usually the case in such environments (Stull, 1992). The NBL was decoupled from the RL in average some 14 hours every day, from about 18:00 to about 8:00 next morning. The RL was advected during this time with a velocity of 10 to 20 m s⁻¹ in the geostrophic wind direction, that is, *ca*. NE. The advection of the MBL and the FT from above the North Atlantic over the (continental) NBL at night therefore could have advanced in the order of 500 km to 1000 km inland from the coast – overnight. Sipaliwini was about 550 km downwind from the coast, given that the wind direction was predominantly NE, especially in the higher levels. Therefore, in most of the area under study, including Sipaliwini, every morning the decay of the NBL led to the entrainment of marine or FT air that had been advected overnight from above the North Atlantic.

The MBL is regularly about 600 m thick; so, if the NBL over land reached about 300 m thickness overnight, the FT in the area under study was around 900 m above the ground every morning. Entrainment of the FT air is slower and more energy consuming than entrainment of a mixed RL. Entrainment of a mixed layer, as the MBL, can be comparatively fast. So a mixing layer about 900 m thick quickly developed over most of the land surface between the coast and Sipaliwini every morning, probably before 10:00 or 11:00. Contributions to the ML were around 20 to 25% from the NBL, 45 to 55% from the RL and 25 to 35% from the FT on normal days. The FT may have included fossil layers forming after a continental ML was advected over the ocean, for example, off the African

coast. According to back trajectory calculations by P. van Velthoven, from the KNMI, air parcels in the Surinamese ML often had been previously in the African or South European boundary layer, as shown in Figure III-8 regarding March 15 (see Appendix 3 for further examples).



Figure III-8. Three 10 day back trajectories ending on March 15 in the Surinamese afternoon mixing layer, and starting near or in the African boundary layer. This has been a collaboration of P. van Velthoven, from the KNMI.

The influence of the land surface on the marine air in the RL began every morning as soon as the NBL decayed, around 8:00 LST. The contact of an air mass to the land surface is a major determining factor for dry deposition, a major sink pathway for many trace gases in the atmosphere, including O₃ and organic acids. Additionally, contact and mixing are conditional for the atmosphere to incorporate and disperse substances and particles emitted at the surface.

The NBL decay before dawn on March 25 through 27 was apparently a consequence of the strong subsidence taking place (Peters, 1998), which was presumably >1 cm s⁻¹. The NBL under the subsidence conditions was probably thinner than usual, and wind shear at its top eventually broke it down long before convection initiated. An additional effect of subsidence was the increase of temperatures, as a consequence of the entrainment of larger amounts of (potentially) warmer FT air. Trace gases and aerosols transported in the FT probably affected the ML concentrations in those days; this is discussed in subsequent sections of this chapter.

Land-sea breeze could have been important at most in the first 20 to 50 km near the coast. In general, sea breeze (due to warming of the air over the land surface) may reach 2 to 5 ms^{-1} , according to Oke (1987), and is usually stronger than the nocturnal land breeze. Provided that mean wind velocities in the lower 2000 m of the troposphere under normal conditions were in the order of 5 to 8 ms^{-1} , at night as well as during daytime, land-sea breeze probably played a minor role in determining the boundary layer dynamics of the coastal areas.

III.2.Results and discussion

In the following subsections, the results of the measurements of CO, O₃ and organic acids are presented. The sampling inlets used for all atmospheric compositional measurements in Sipaliwini were 8 m above ground, upwind from the station of the MSS and from the rest of the houses and huts of the village. On a dry season day in a treeless flat area like Sipaliwini, most of the concentration gradient occurs in the first 3 to 5 meters above the ground surface. Measurements made above about 4 m differ from the average ML value in less than 10%. During the morning hours, intensive entrainment of air from a layer that may have very different properties from those of the developing ML, has an important influence on the ML concentrations of measured species. The afternoon hours, during which the ML is in a *quasi* equilibrium because Z_i remains essentially constant at its maximum (Stull, 1992), are of particular value for ground based observations because of the representativity of the data.

III.2.1. CO

At Sipaliwini, an infrared spectrophotometric instrument was used to measure CO concentrations; readings were recorded automatically every minute. Calibration of the 0 point was made every 30 minutes and calibration with standard gases once a day. Uncertainty was determined by the drift of the instrument during the day, and amounted to ± 20 nmol mol⁻¹. At Alliance (21-30 March), CO concentrations were measured automatically every 15 minutes by means of a reduction-gas-detector (Trace Analytical); uncertainty for the individual data were in the order of ± 5 nmol mol⁻¹. Further analytical details can be found in the experimental part (chapter II).

III.2.1.1.The diel cycle of CO.

The diel cycles of the CO values in Sipaliwini and at Alliance are shown in Figure III-9; they were characterized by values between 100 and 150 nmol mol^{-1} at daytime and significantly higher and much more variable at night. Plots for individual days are to be found in Appendix 2. The existence of a stable NBL and the proliferation of local CO sources – cooking fires, cigarettes, biomass burning, etc.–- near the sites during the night hours, are

the reasons for the nocturnal high variability and high values in general. Afternoon values showed less variability, and were the lowest in the diel cycle.



Figure III-9. Hourly means of CO averaged over the whole measurement period, for Alliance and Sipaliwini. – Error bars are 1sd. Data are from days with simultaneous measurements at both sites.

Because the daytime values were representative of a well mixed – and mixing– BL, nearby sources affected them only little. Note how the standard deviation is much smaller for daytime values.

III.2.1.2. Day to day variation of the CO levels.

Figure III-10 shows the afternoon averages (from 12:00 to 17:00 LST) of the CO VMR at Alliance and Sipaliwini. Values were usually slightly higher in Sipaliwini. Average day to day variability was similar at both sites: 20 nmol mol⁻¹day⁻¹ in Alliance and 17 nmol mol⁻¹day⁻¹ in Sipaliwini. Because of the uncertainty of the measurements (Sipaliwini, ± 20 nmol mol⁻¹; Alliance, ± 5 nmol mol⁻¹), a significant difference between the sites cannot be

assessed from the data. The high CO levels in Alliance on March 22 were apparently related to biomass burning near the measurement site (personal communication, J. Romero; Gregoire *et al.*, 1999).



Figure III-10. Afternoon average VMRs of CO at Alliance and Sipaliwini.

Good agreement of the averages of the ground based and the airborne CO measurements was found. Overall afternoon averages for Sipaliwini and Alliance were 125 ± 25 nmol mol⁻¹ (SD; N = 90; from hourly means); the airborne data yield an overall mean of 121 ± 32 nmol mol⁻¹ for the boundary layer (Pöschl *et al.*, 2001).

Biomass burning was apparently not an important source of CO at a regional scale. Pöschl *et al.* (2001) discard a dominant local influence of biomass burning on the grounds that they did not find a significant correlation among the CO, acetonitrile and CO_2 airborne data. Additionally, Gregoire *et al.* (1999) report detecting fires by means of AVHRR (Advanced Very High Resolution Radiometer) satellite data mainly to the West (downwind) of the study area, the nearest fires being at the coast near Wageningen, in Surinam.

Williams et al. (2001) reported an increase rate for the CO mixing ratios below 2000 m during the LBA-CLAIRE campaign, of 29 pmol mol⁻¹ km⁻¹ in the N to S direction. This was obtained from airborne measurements made over Surinam. As they mention, an increase was expected due to oxidation of locally emitted VOCs. Crutzen et al. (1985) had already discussed the likelihood of such a positive CO gradient over the rainforest in this region, arriving to an estimate of 30 nmol mol⁻¹ day⁻¹, equivalent to an increase of *ca*. 13 nmol mol⁻¹ in 10 hours at a fixed location. Ten hours was the most that the BL in Sipaliwini could accumulate of influence from the land surface, as discussed regarding the BL dynamics in the area. The increase reported by Williams et al. (2001) is equivalent to 21 pmol mol⁻¹ km⁻¹ in the NE wind direction, that is, to about 6 nmol mol⁻¹ in 10 hours at a location as Sipaliwini, if a mean BL wind speed of 8m s^{-1} is assumed. This is about half of that estimated by Crutzen et al. (1985). Unfortunately, the uncertainty of the measurements in Sipaliwini was too high to assess an increase of 6 nmol mol^{-1} . So the observation of Williams et al. (2001) cannot be hereby confirmed. However, an average variability of about 20 nmol mol^{$^{-1}$} dav^{$^{-1}$} (or 8 nmol mol^{$^{-1}$} in 10 hours) has been estimated for both sites. which is similar to the increase estimate of Williams et al. (2001), and should be considered as an uncertainty term.

III.2.2.Ozone

Ozone was measured at all sites by means of automatic commercial instruments using ultraviolet absorption detection (see analytical details in experimental part, chapter II). A value every 12 seconds was obtained in Sipaliwini. One-minute values were recorded at Alliance (J. Romero and E. Fernández, IVIC), as well as in Petit Saut and Balbina, sites from which D. Serca and C. Galy-Lacaux (OMP, Toulouse), and J. Kesselmeier (MPIC, Biogeochemistry department), respectively, have kindly provided data. In general, uncertainty was ± 2 nmol mol⁻¹ and the instrument's detection limit was 2 nmol mol⁻¹.

III.2.2.1. The diel cycle of ozone

The average diel cycle of O_3 in Sipaliwini is presented in Figure III-11. In Sipaliwini, early morning ozone levels were usually below the detection limit of the instrument, until shortly after the wind started picking up. A sharp rise in the ozone level (in average *ca*. 4 nmol

mol⁻¹ h⁻¹) was associated to the start of turbulence (seen in the wind speed data); as said before, turbulence usually started before 9:00 LST, and on some days started earlier than 6:00 LST. The ozone maximum generally occurred between 10:00 and 13:00 LST. In the afternoon, ozone levels showed a regular pattern. After the maximum, a fairly reproducible decrease occurred until around 18:00 LST (in average -0.95 nmol mol⁻¹ hr⁻¹; sd = 0.31; N = 10 days; datasets from 4 days were disregarded due to unusual concentration surges or incompleteness). During the late afternoon hours, ozone levels generally showed rapid decay (in average *ca.* -2 nmol mol⁻¹ h⁻¹). This decay is clearly associated to the development of the NBL.



Figure III-11. Averages of hourly means for O_3 in Sipaliwini. Error bars are 1 **sd**. Averaged days are March 14-21 and 24-27. The detection limit of the instrument was 2 nmol mol⁻¹; averages below this value include some hourly means that were larger than the detection limit.

Diverse variations of the O_3 levels related to momentaneous meteorological effects were observed, *e.g.* concentration surges associated to showers (23.03 around 13:00 and 19:00) or to nocturnal wind gusts (most nights), high evening (22 and 23.03) or early morning values (26 and 27.03) associated to untypically high turbulence, etc. For reasons of space,
these are not described or discussed here. However, Appendix 2 contains plots of the combined data of CO, O_3 and wind speed; there, these effects are to be clearly seen, if the reader wishes. Furthermore, data from March 13 (an incomplete data set) and March 22-23 (with unusual increases of O_3 levels in late afternoon, linked to wind gusts and/or showers) have not been included in Figure III-11. For a similar plot considering all available data, the reader is referred to Appendix 2.

III.2.2.2.Day to day variation of the ozone levels.

Figure III-12 shows the O₃ afternoon (12:00 to 17:00 LST) averages for Alliance, Petit Saut, and Sipaliwini from March 2 to 28.



Figure III-12. Daily O₃ afternoon average VMRs at the three sites North of the ITCZ during the LBA-CLAIRE campaign. Data for Alliance were kindly provided by J. Romero and E. Fernández (IVIC), and for Petit Saut by D. Serca and C. Galy-Lacaux (Laboratoire d'Aérologie, OMP, Toulouse).

The three data sets in Figure III-12 show the same variation pattern, even though the data from Sipaliwini show lower levels and some smoothing with respect to the other sites. The

three variation patterns apparently have a day to day coupling, that is, there is not a 1 day delay in the variations in Sipaliwini with respect to the other sites.

III.2.2.3.Day to day covariation of O₃ and CO levels.

In Figure III-13 it is seen that the levels of O_3 and CO in Sipaliwini showed similar variation patterns. There is in fact significant correlation (R = 0.75; N = 14; P = 0.01); Figure III-14 shows that there are two well differentiated groups of points, representing high and low levels. The afternoon averages of CO and O_3 near the coast showed the same day to day variation pattern as inland throughout the period of the study.

The day to day variation patterns of CO and O_3 near the coast were the same as those observed 550 km inland, in Siplaliwini. This suggests long range transport of these species as the main variability factor and their key supply process in the region.



Figure III-13. Average afternoon values for O₃ and CO in Sipaliwini from March 13 to 27, 1998.



Figure III-14. Ozone vs. CO in Sipaliwini. Daily afternoon average values. Correlation is significant at 95% level (R = 0.75; N = 14; P = 0.01; slope = 0.13).

Probably, the higher O_3 and CO levels were due to advection of contaminated air parcels from the Southern European continent, Northwest Africa or North America. Ten-day back trajectory plots for several end days during the sampling period indicate advection of air parcels from the Southwestern European and / or Northwest African boundary layer (see in Appendix 3) to Surinam. In particular, most of the trajectories ending in Sipaliwini started in the Northwest African BL.

According to that discussed regarding the BL in the area under study, the air parcels constituting it were advected every (previous) night over the continental NBL from above the North Atlantic ocean. The day to day coupling of the variation patterns for CO and O_3 of Sipaliwini with those of the coastal sites further supports this. Apparently, the air parcels incorporated each day into the mixing layer at the coastal sites had similar characteristics as the air parcels entrained into the ML several hundred kilometers inland, for example, in Sipaliwini. The differences resided rather in the time of contact of the air parcels to the land surface; near the coast this was minimal and constant, while in Sipaliwini it increased thoughout the day.

III.2.2.4. Estimations of the loss of ozone in the BL in Sipaliwini.

The significantly lower O_3 values inland as compared to the sites near the coast imply a net loss of ozone in the BL in the area of Sipaliwini. It is known that loss of ozone is more intensive over the land surface than over the ocean; the major loss processes, as well as likely production processes, are discussed in the next section. Here, the net loss shall be quantified. Because it is the consequence of a variety of processes, the net loss rate will be treated as if of order 1 with respect to the ozone concentration, that is,

$$k_l = -\ln([O_3]_t / [O_3]_0) / \Delta t$$

The concentration differences between Sipaliwini and the coastal sites are considered to be the consequence of a difference in time spent by the air over the land surface. The value of k_i is obtained from these differences and the afternoon means of O₃ for the two sites. An estimate of k_i was obtained for each day, then they were averaged for each site. Relevant information is shown in Table III-3. The result is similar with respect to both sites near the coast, that is, $(5 \pm 2) \% h^{-1}$ when considering Petit Saut and $(9 \pm 3) \% h^{-1}$ when considering Alliance (the uncertainty is the standard deviation of the estimates for individual days).

Table III-3 Estimation of the loss rate constant \mathbf{k}_{l} in Sipaliwini from the differences in ozone concentrations with respect to the sites near the coast.

Location	Distance from the coast / km	Estimated hours over the land surface	Mean calculated value of $k_l \pm s / h^{-1}$				
Alliance *	0	0	0.09 ± 0.03				
Petit Saut **	<i>ca.</i> 40	<i>ca.</i> 1.5	0.05 ± 0.02				
Sipaliwini was <i>ca.</i> 550 km downwind from the coast, that is, <i>ca.</i> 6.5 hours away at 8 ms ⁻¹							
* All 7 afternoon averages considered. ** 13 data of 15 considered.							

The loss rate of O_3 in Sipaliwini was additionally estimated from the concentration decrease rate during the afternoon hours, when the mixing layer depth (Z_i) remained essentially constant, that is, from *ca*. 13:00 to *ca*. 17:00 LST. During these hours, whatever loss processes that occurred affected an air layer with a constant thickness, and entrainment of air from superior layers practically did not take place. As shown before, there was an O_3 concentration decrease during these hours every day that was approximately linear in time; afternoon mean values of the decrease ratio $[O_3]_t/[O_3]_0$ were obtained for each day, in order to calculate the day's k_l . Data from afternoons in which surges in the ozone concentrations associated to wind gusts occurred (evidently originating in downdrafts that entrained ozone rich air from superior layers) were not considered. Data from days in which a transition from high ozone levels to low levels, or *viceversa*, occurred, were also excluded. Table III-4 contains the mean afternoon hourly decrease ratios $[O_3]_t/[O_3]_0$, obtained from hourly evaluations from 12:00 to 17:00 LST on each day, and the criteria used to exclude the data or use them. Days in which a transition to higher levels or to lower levels occurred yielded, respectively, lower or higher decrease ratios than other days.

DATE	[O ₃] _t / [O ₃] ₀	Criteria	DATE	[O ₃] _t / [O ₃] ₀	Criteria
13.03	_	incomplete	21.03	_	incomplete
14.03	0.953	OK	22.03	0.961	OK
15.03	0.958	ОК	23.03	0.988	wind gusts / rain
16.03	0.914	high -> low transition	24.03	0.980	low -> high transition
17.03	0.901	high -> low transition	25.03	0.940	OK
18.03	0.946	ОК	26.03	0.938	OK
19.03	0.946	ОК	27.03	0.922	high -> low transition
20.03	0.951	ОК	MEAN	0.949	sd = 0.009 ; N = 8

Table III-4. Ozone afternoon decrease ratios in Sipaliwini.

The loss rate of O₃ upwind from Sipaliwini obtained from the afternoon data is

 $k_l = -\ln(0.949) / (1 \text{ hour }) = (0.05 \pm 0.01) h^{-1};$

that is a net loss rate of $(5 \pm 1) \% h^{-1}$, a similar result as that obtained previously, with a lower uncertainty.

III.2.2.5.Source and sink processes for ozone in the area under study.

The key supply process of O_3 in the area was the advection of air parcels from above the North Atlantic ocean and their subsequent entrainment into the ML; advection supplied each day's background level, upon which further local source and sink processes had an effect.

Source processes

During the afternoon hours, when entrainment had ceased, the major possible ozone source process was production by oxidation of VOCs and CO present in the air. This could have represented a source or a sink for O₃, depending on the NO_x concentrations. NO_x levels beyond *ca*. 20 pmol mol⁻¹ can lead to a O₃ productive chemistry in the troposphere. Unfortunately, no meaningful NO_x concentration data were produced during the LBA-CLAIRE campaign, so the levels in the area at the time can at best be estimated approximately, based on data from similar environments. During the ABLE experiments over the Amazon basin, NO levels between 10 and 60 pmol mol⁻¹ were recorded over the rainforest during the dry season (Torres and Buchan, 1988) and around 11 pmol mol⁻¹ in coastal regions, outside air directly affected by biomass burning. In the wet season, NO levels were low enough for oxidative chemistry to have represented a net sink of O₃ (Jacob and Wofsy, 1990).

As concerns the air parcels advected over the NBL, in the marine BL, levels below 10 pmol mol^{-1} NO are usual (*e.g.* Heikes *et al.*, 1996); advection of air masses with high NO_x levels from the marine BL can reasonably be discarded in the area under study. The same cannot be said regarding the free troposphere (FT), however. As already explained, in the area under study around 30% of the air in each day's BL was entrained from the FT. Thermal dissociation of PAN, incorporated from the FT, was a possible important source of NO, especially if smoke or contamination plumes influenced the local air composition, as seems to be the case. Heikes *et al.* (1996) observed this in remote marine environments, where entrainment is comparatively unimportant.

Soil NO emissions were seemingly unimportant for the ozone in Sipaliwini. Jacob and Wofsy (1988) found soil emissions to account for the background concentrations during the

dry season ABLE-2A campaign. Kaplan *et al.* (1988) found soil emissions of NO to average $5.2 \pm 1.7 * 10^{10}$ molecules cm⁻² s⁻¹ near Manaus, in the Ducke forest reserve, during the dry season, while Bakwin *et al.* (1990a) measured about 1/5 of that during the rainy season, for several samples and locations of the dominant kind of soil in the central Amazon region. Jacob and Wofsy (1990) estimated that no more than 20% of soil NO emissions get to the Amazon boundary layer, while the rest reacts and deposits to the vegetation before exiting the canopy. 20% of the dry season emission amounts to 10 pmol mol⁻¹ hourly input for $Z_i = 1400$ m; that is a large amount of NO. However, deposition of NO_z balanced out with the emissions (Bakwin *et al.*, 1990b), so a significant buildup did not occur. A similar situation probably occurred during LBA-CLAIRE in the forested areas upwind from Sipaliwini, even though immediately upwind from Sipaliwini was an extension of savanna and mixed (low) vegetation about 30 to 50 km long.

Emissions of NO in low vegetation areas are readily incorporated into the mixing layer because there is less dry deposition to the vegetation (as NO₂) and the mixing is more intensive due to stronger heating of the ground. The savanna area upwind from Sipaliwini presumably could have provided enough NO_x to raise the levels in air arriving in Sipaliwini by 20 pmol mol⁻¹, at an emission rate of 5.2×10^{10} molecules cm⁻² s⁻¹. Model calculations led by R. Von Kuhlmann (personal communication, 1999) showed that the ozone levels seen in Sipaliwini could not have increased in more than 20% due to this NO_x input, because it took place so near upwind from Sipaliwini. A greater effect should be expected further downwind, however; furthermore, more savanna area exists downwind from Sipaliwini, so O₃ levels probably increased significantly.

Given that O_3 and CO were mainly advected to the site, significant amounts of NO_x or PAN could have also been advected to the site. As shown in Table III-4, the O_3 loss rate on the days with highest mixing ratios was not lower than on other days (*ca.* 5.5% h^{-1} as compared to usual *ca.* 5% h^{-1}). This suggests that NO_x levels in the imported air parcels were never high enough to make the VOC oxidation chemistry significantly ozone productive, and that the highest O_3 levels in the period were not due to larger mixing ratios of NO_x, nor to local production. Therefore, the oxidation chemistry of VOCs in the area under study was apparently not an important O_3 production process during the sampling period.

Loss processes

The major loss processes for ozone in the area were deposition and reactions; the latter could have taken place in the gas phase and in the aqueous phase, namely in cloud droplets. It is not clear at this point how important loss by reaction in clouds could have been. According to calculations by Lelieveld and Crutzen (1990), cloud chemistry may be responsible for the destruction of as much as 30% of tropospheric O₃ on a global scale. Later calculations by Liang and Jacob (1997), assign cloud chemistry 3% or less of total loss in tropical and midlatitude regions. Despite the fact that the period of measurements was not rainy, formation of small cumuli was abundant. So cloud chemistry may have represented a sink for O₃ in the incoming air masses, though it is uncertain how great.

Reactions with VOCs and photolysis under low NO_x conditions upwind from Sipaliwini were possibly responsible for part of the O₃ loss. Table III-5 shows the main reaction sink processes for ozone up to Sipaliwini, during the LBA-CLAIRE campaign. Isoprene was the major VOC reacting with ozone, as calculated from the concentration data obtained by airborne measurements carried out using the Proton Transfer Reaction Mass Spectrometry (PTRMS) technique (Warneke, 1998; Warneke *et al.*, 2001). According to these measurements, isoprene was the most abundant hydrocarbon in the CML during the LBA-CLAIRE campaign, with VMRs in the order of 2 - 4 nmol mol⁻¹ in the latitude range of Sipaliwini. Other NMHC were found in lower concentrations, such that they could only have a minor role in ozone loss. Acetylene, ethene and propene, for instance, were in general well below 500 pmol mol⁻¹ (personal communication, Bert Scheeren, IMAU, Utrecht).

Photolysis of O_3 leading to formation of HO radicals, which initiate the oxidation of CO, methane and other hydrocarbons, was another important sink pathway. It amounted to somewhat less than 1% h^{-1} (calculation details in Table III-5).

Reaction of O_3 with HO_2 should also be considered. Self reaction of HO_2 produces H_2O_2 . If reactions with other peroxy radicals are ignored, an estimate of the maximum concentration of HO_2 can be derived from

$$d[H_2O_2]/dt = k_R [HO_2]^2 - k_{dep} [H_2O_2] - J [H_2O_2]$$

The H₂O₂ increase seen during the early afternoon hours in Sipaliwini (personal communication, Dirk Grossmann, MPI) was less than *ca*. 30 pmol mol⁻¹ h⁻¹. H₂O₂ dry deposition over a boreal forest was found to be 5 cm s⁻¹ at daytime (Hall and Clayborn, 1997) and about 1 cm s⁻¹ at night, essentially the same value as found by Heikes *et al.* (1996) over the ocean. Even though 5 cm s⁻¹ is a high deposition velocity, and it was measured over a boreal forest, it is the best approximation found for a tropical forest, which could probably have higher values. Assuming a similar V_d for H₂O₂ upwind from Sipaliwini:

$$k_{dep} = V_{dep} / CML$$
 height = 3.6 x 10⁻⁵s⁻¹.

SINKS	Mechanism/conditions	% h ⁻¹		
Reaction with	$[isoprene] = 2 - 4 nmol mol^{-1}$	0.21-		
isoprene	$k = 12.8 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	0.49		
	(298 K) (Atkinson, 1997)			
Photolysis	$J = -1.5 \times 10^{-5} s^{-1}$			
	fraction of the O (¹ D) reacting with $H_2O = -0.06$			
Methylvinylketone	$[MVK] = \sim 2 \text{ nmol mol}^{-1}$	~0.09		
	$k = 5.4 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$			
	(298 K) (Neeb <i>et al.</i> , 1998)			
Reaction with HO ₂	$[HO_2] = \sim 15 \text{ pmol mol}^{-1}$	0.35		
	$k = 2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (298 K)			
	(Atkinson <i>et al.</i> , 1997)			
TOTAL SINK BY REACT	ΓIONS:	~ 1.5		

Table III-5. Estimates of reaction sink processes of O₃ in Sipaliwini.

For $k_R = 4.8 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹ (at 298 K, 1013 mbar and 1.2% air water content; Stockwell, 1995), $k_{dep} = -3.6 \times 10^{-5} \text{s}^{-1}$, and $[H_2O_2] = -550 \text{ pmol mol}^{-1}$ (Dirk Grossmann, personal communication), and $J = -5 \times 10^{-6} \text{ s}^{-1}$ (for the dissociation of H_2O_2),

$$[HO_2] = \sim 16 \text{ pmol mol}^{-1}$$
,

so the loss of O₃ through this process amounted to around 0.35% h^{-1} . If the V_d of H₂O₂ over the tropical forest had been only 2 cm s⁻¹ instead of the assumed 5 cm s⁻¹, the resulting loss would be 0.18% h^{-1} , a similar value.

So the loss of O_3 by reaction in the area may have been similar to 1.5 % h^{-1} .

Loss of O₃ by deposition

Wet deposition plays a negligible role for O₃. Dry deposition is a major ozone sink, especially over vegetated landscapes, given the high rate of stomatal uptake (*e.g.* Padro, 1996; Pleim *et al.*, 1999). Deposition velocities were not measured during the LBA-CLAIRE campaign, so measurements in similar environments shall have to be used to make an estimate of the loss of ozone by deposition. Highest O₃ deposition velocities over vegetated landscapes measured by eddy correlation have been in the order of 1.7 to 2 cm s⁻¹ (*e.g.* Padro, 1996); values nearing 1 cm s⁻¹ have been more frequently reported. A V_d of 1 cm s⁻¹ to 1.5 cm s⁻¹ in Sipaliwini during the afternoon hours is equivalent to between 2.6% h⁻¹ and 3.9 % h⁻¹ ozone loss. The uncertainty of the deposition term is similar in magnitude to the reaction term.

The estimated loss processes add up to between 4.1 % h^{-1} and 5.4 % h^{-1} . Loss by reaction in cloud droplets has not been considered so far; if loss by reaction in cloud droplets amounted to between 3% and 30% of total loss, then the estimate for total loss is between 4.2 % h^{-1} and 7.7 % h^{-1} . This is close to the (5 ± 1) % h^{-1} net loss that has been previously estimated from the measurements.

III.2.3. Formic and acetic acids

Organic acids in the gas phase were sampled and measured only in Sipaliwini; those found consistently in measurable concentrations were acetic and formic acids. Additionally, pyruvic, oxalic and propionic were found in detectable concentrations in some samples, though usually near or below the LOD (about LOD see section II.1.5). Pyruvic acid was usually present in such small concentrations possibly due to its lability in the daytime. Oxalic acid was found consistently in the samples, but usually near the LOD, so no quantitative information could be derived; its equivalent gas phase VMR was usually below

about 0.3 nmol mol⁻¹. Inorganic species as nitrate and sulfate were found in the samples in concentrations near the LOD, and were usually not quantifiable. The data presented and discussed here will be those regarding formic and acetic acids in the gas phase.

The samples were collected from the gas phase 8 m above the ground; the acids were captured by uptake into the condensing atmospheric water with an efficiency near 95% (see the Experimental Part, chapter II). Acetic and formic acids had average boundary layer VMRs of 1.5 nmol mol⁻¹ and 1.2 nmol mol⁻¹, respectively, between 12:00 and 17:00 LST.

III.2.3.1. The diel cycles of formic and acetic acids.

The average diel cycles of HCOOH and CH₃COOH are shown in Figure III-15. The main features are ascending VMRs from about 7:00 LST until after midday, approximately constant values from then until around 17:00, and rapid decay after that until around 21:00 LST for CH₃COOH and until around 23:00 for HCOOH. Early morning and late night values in the figure are single values, and so do not have error bars representing the dispersion of the data. Typical night time VMRs for both acids were similar to 0.5 nmol mol⁻¹ or lower, often below the LOD of the employed method. The average morning increase rate was around 85 pmol mol⁻¹ h⁻¹ for both acids. Plots of data corresponding to individual days are shown in Appendix 2. The decay of the VMRs in the late afternoon on individual days started between 16:30 and 18:00 LST, as in the case of O₃.

There was not a clear connection between the morning VMR increase of the organic acids and that of O_3 . There was an apparent relationship to the increase of turbulence, though not the same as for O_3 . On March 26 and 27, wind speed and O_3 levels increased significantly before dawn, but the organic acids VMRs did not until after 8:00. March 24 had low morning wind speed and low O_3 levels until 9:00 LST, and the acids' VMRs were still around 0.5 nmol mol⁻¹ at 9:00 LST, unusually low for that time of the day.

The acids' maxima on individual days occurred in the early or mid afternoon, and show no clear connection to the maxima of wind speed or of O_3 . The average O_3 and wind maxima occurred just before midday, this is, about 2 hours earlier than that of the acids. On March 26 and 27, the daily maximum O_3 level was reached around 10:00 LST and that of wind speed about 2 hours later; the increase of the acids' levels in those 2 hours was of *ca*. 0.5

nmol mol⁻¹. In general, once the O₃ levels and wind speed started to decrease in the afternoon, those of the acids kept approximately constant for several hours. The decrease of the acids' levels at late afternoon coincided with the sharp decrease in wind speed and O₃ levels, when the NBL developed.



Figure III-15. Overall means of hourly averaged VMRs of HCOOH and CH₃COOH in Sipaliwini from March 19 to 27. – Error bars are 1**sd** ; points without error bars are single values.

The clear coupling of the O_3 and the wind speed diel cycles, particularly in the morning hours, is an indicator of the downmixing of O_3 from the residual layer (RL) once the NBL decays every morning. A similar morning increase tendency was observed for HCOOH and CH₃COOH in Sipaliwini, but it was delayed in at least 1 hour, as compared to O_3 and wind speed. Thus the RL was clearly not so important a reservoir of the organic acids as it was of O_3 . This is in agreement with the RL being constituted by air parcels advected overnight from the marine BL above the North Atlantic; the MBL has usually low levels of water soluble and water reactive trace gases, due to cloud processing and wet deposition. The FT, in turn, probably contained significant amounts of organic acids, especially during periods when transport of contaminated air parcels from North America, Southern Europe and Northwest Africa took place. Thus, entrained FT air was a likely source of organic acids in the area. As discussed in previous sections regarding the BL dynamics in the area, FT air was probably entrained during late morning and early afternoon hours. This is in agreement with the delayed response of the organic acids levels to the increase of turbulence. Furthermore, the days when strong regional subsidence occurred – March 25 through 28 – coincided with the highest increase rates and highest maxima of the organic acids in the sampling period. Subsidence necessarily augmented the proportion of FT air being entrained into the ML on those days. This and other likely source processes are further discussed in a later section.

The sharp decrease of the acids' VMRs in the late afternoon and early evening, coinciding with fast depletion of O_3 , was probably due to deposition after the NBL had developed above the level of the sampling inlet. According to Hartmann *et al.* (1991) and Sanhueza *et al.* (1992), these organic acids have similar V_d (about 1 cm s⁻¹) to O_3 in the newly formed NBL.

Rainfall lowered the VMR of the organic acids for one or two hours after each event in *ca*. 10% to 40%. This suggests that dry deposition of these acids in tropical forests under wet conditions is significantly more efficient. However, as mentioned before, it rained seldom in the area.

III.2.3.2.Day to day variation of the HCOOH an CH₃COOH levels.

The day to day variation of the HCOOH and CH₃COOH afternoon levels is shown in Figure III-16. Levels decreased toward March 19, kept approximately constant until March 23, and increased again toward March 26 and 27, when a period of strong regional subsidence took place. From March 20 to 23, CH₃COOH levels were slightly higher than those of HCOOH; the rest of the time, HCOOH was more abundant. The sporadic rain events during the sampling period were not determinant to the VMRs of the organic acids in Sipaliwini. An example is March 23, when three rain events took place; though the day's average VMRs were below 1 nmol mol⁻¹, they did not fall out of the general variation trend.



Figure III-16. Day to day variation of HCOOH and CH₃COOH. Data are the afternoon average VMRs (12:00 - 17:00 LST). Error bars are 1 sd; they are the indicator for variability during the averaged hours.

Formic and acetic acids had a day to day variation pattern similar to that of O_3 . The correlation of the afternoon average data for O_3 with those of HCOOH (R = 0.78) and CH₃COOH (R = 0.63) was significant at the 95% and 85% confidence levels respectively. This covariation of the organic acids levels with the O_3 levels during the sampling period again suggests the likelihood of imports of organic acids. Smoke and contamination plumes advected over the MBL develop high levels of organic acids and of O_3 just as well (Heikes *et al.*, 1996; Talbot *et al.*,1997 and 1999; Mauzerall *et al.*, 1998). Higher O_3 levels may have also contributed to increased local production of the organic acids, of course; this is discussed in a later section.

III.2.3.3.The [HCOOH] / [CH₃COOH] ratio.

The diel cycle.

Ratios of formic to acetic acid varied from around 1.6 during morning hours to *ca*. 0.8 in the evening. The decrease tendency persisted throughout the night, though not so

pronounced. The hourly averaged ratios for the period from March 19 to 27 are shown in Figure III-17. The data from most individual days showed a variation pattern similar to the average seen there; plots of these data are to be found in Appendix 2.



Figure III-17. Hourly averaged HCOOH to CH3COOH ratios. Early morning values are not included while too few to build a representative average; available ones are similar to nocturnal values. Average variation was of -0.06 h^{-1} . Error bars are 1**sd**.

There was a clear connection between the early morning increase of the ratio and the decay of the NBL. Data corresponding to hours before 7:00 LST were few and an hourly mean value could not be built with them; however, they were the lowest values. Days with low or delayed early morning turbulence, as March 23 and 24, showed a slow increase of the HCOOH / CH₃COOH values, in clear contrast to the usual observations. So, also in the case of this ratio, the RL seemingly provided each day's background values. The clear daily decrease tendency in the ratio values was evidently due to faster increase of the CH₃COOH VMR in the morning, as compared to HCOOH, and later to faster loss of HCOOH. Results from several previous works in remote areas lead to a similar diel variation of the ratio (*e.g.* Arlander *et al.*, 1990; Talbot *et al.*, 1988; Martin *et al.*, 1991; Hartmann *et al.*, 1991).

Rain events had a transitory effect on the diel variation pattern of the HCOOH / CH₃COOH ratio. As shown in Figure III-18, rain events on March 23 lowered the HCOOH / CH₃COOH ratios for a couple of hours after the end of each event. Similar observations have been made by Hartmann *et al.* (1991) and Sanhueza *et al.* (1992, 1996).



Figure III-18. Variation of the HCOOH / CH₃COOH ratio on March 23. Rain events were followed by lower ratio values.

As explained by Andreae *et al.* (1988), the observed effect of wet conditions is probably a consequence of the lower water solubility of CH₃COOH at pH values above 4. Rainwater in Sipaliwini had pH values above 4. The effective Henry distribution coefficient is given by

$$K_{\text{Heff}} = K_{\text{H}} (1 + K_{a} / [\text{H}^{+}])$$

where K_a is the dissociation constant of the acid and K_H is the simple Henry coefficient. For HCOOH and CH₃COOH the K_H are 5400 and 5200 respectively, while the K_a are 1.77 * 10^{-4} and $1.75*10^{-5}$ respectively. Table III-6 shows the K_{Heff} values for the two acids at different pH values. As shown in the last row, the solubility of formic acid is several times

that of acetic acid for pH values beyond 4, so uptake into the water film on wet vegetation

would be more effective than for acetic acid.

Table III-6. Values of the K_{Heff} for HCOOH and CH_3COOH at 298 K , at different pH values, and the water solubility relation of HCOOH to CH_3COOH . Units of K_{Heff} are mol dm⁻³ atm.

рН =	1	2	3	4	5	6	7
НСООН	5410	5496	6356	14958	100980	961200	9563400
СН₃СООН	5201	5209	5291	6110	14300	96200	915200
relation	1.0	1.1	1.2	2.4	7.1	10.0	10.4

The observed consistent decrease in the HCOOH / CH₃COOH ratio from morning to evening points to slower loss of CH₃COOH and / or faster CH₃COOH production. Probably, HCOOH had more efficient loss processes than CH₃COOH, as faster uptake into water films and droplets, and subsequent oxidation by HO radicals. Added to this, CH₃COOH has faster production channels, like HO initiated oxidation of isoprene and other olefins as fast production pathways for the peroxy radicals that lead to formation of CH₃COOH, in contrast to HCOOH production by ozonolysis, which is slower and dependent on the O₃ levels.

Day to day variation.

It has been shown that the day to day variation patterns of formic and acetic acids are highly correlated to that of O_3 . Figure III-19 shows that the variation pattern of the HCOOH / CH₃COOH ratio is just as well very similar to that of O_3 . Correlation of afternoon averages of the ratio data with those of O_3 was 0.74 (N = 10); it was significant at the 95% level of confidence. The afternoon averages of the ratio were between about 0.7 and 1.8, with values below 1 from March 20 through 23. The lowest daily value was 0.7, on March 22, a day without apparent rainfall in the area near Sipaliwini. The highest value of the ratio was 1.8, on March 26, one of the days with strong regional subsidence, and the hottest of the period.

As in the case of the VMRs of the acids, rain did not have noticeable effect on the day to day variation pattern of the HCOOH / CH₃COOH ratio. Days with drizzle or rain events

were March 21 and 23. March 22 was a dry day, but the value of the ratio was the lowest in the period. As it seems, the rains were too sporadic to keep a permanent water film on the vegetation in the area during any single day, so wet conditions did not exist as such; only short lasting wetness after sporadic showers.



Figure III-19. Ozone, formic and acetic acids and the HCOOH / CH₃COOH ratio; afternoon average data from Sipaliwini.

Several works have shown that low HCOOH / CH₃COOH ratios are obtained in biomass burning smoke plumes, and the acids produced in fires easily yield ratios of 0.1 (*e.g.* Hartmann, 1990; Talbot *et al.*, 1988). Biomass burning can cause this effect at regional scales (Lefer *et al.*, 1994). Smoke plumes from biomass burning are evidently marked by large concentrations of CO, produced in the fires. Coincidence of low HCOOH / CH₃COOH ratios and high CO levels was observed occasionally in Sipaliwini at night and early evening; it was apparently related to small but highly concentrated smoke plumes from nearby cooking fires and cigarettes, reaching the sampling inlet. At daytime, none of this happened. Other works have shown that air affected by biomass burning smoke can very well show HCOOH / CH₃COOH ratio values above 1, particularly when the plumes have aged for a few days. Talbot *et al.* (1997, 1999) reported smoke plumes above the remote marine BL with higher levels of HCOOH than CH₃COOH. Similar observations have been reported previously by Sanhueza *et al.* (1996) and Helas *et al.* (1992); even though their measurements were, respectively, likely and surely influenced by biomass burning, the HCOOH levels were higher than those of CH₃COOH. Thus, the coincidence of high HCOOH / CH₃COOH ratio values with high O₃, CO and organic acids VMRs does not preclude, but rather supports, the probability of the connection of the high O₃ and acids levels with long range transport of contaminated air parcels.

III.2.3.4. Source and sink processes of formic and acetic acids.

The major sink processes of formic and acetic acids in the mixed layer are known to be wet and dry deposition. Of these, only dry deposition was significant during the sampling period. Increased dry deposition related to wet conditions can be precluded, as rain and drizzle events were sporadic. Velocities of deposition for these acids have been estimated by Hartmann *et al.* (1991) to be similar to 1 cm s⁻¹, which supposes an afternoon loss rate of 2.6% in the hour for $Z_i = 1400$ m.

The major possible source processes of formic and acetic acids in Surinam were direct emission by local ecosystems, local gas phase chemical production and imports. Primary emission by plants has been mentioned in the introduction; several works show results that seem to imply direct emission of HCOOH and CH₃COOH by vegetation (Talbot *et al.*, 1990a; Hofmann *et al.*, 1997; Kesselmeier *et al.*, 1997 and 1998; Martin *et al.* 1999). Though Talbot *et al.*(1990) estimated that the biogenic emission of formic and acetic acids in the Amazon forest was not significant, others (Bode *et al.*, 1997; Kesselmeier *et al.*, 1998; Martin *et al.*, 1999) propose an important contribution of vegetation to the tropospheric budget of these acids. Gabriel and collaborators (Gabriel, Doctoral Thesis, 1997) reported a relation of the acidity of apoplastic fluid in plants to insolation and heat, which would conduce to increased direct emission of the acids during the warmest period of the day. The hottest days in Sipaliwini were March 26 and 27; the VMRs of the acids were also highest on these days. The likelihood of imports of O_3 , CO and organic acids has been mentioned in several occasions in previous sections; the clear coincidence of the day to day variation of the VMRs strongly supports long range transport of contaminated air masses as a source process for the organic acids in the area. The comparatively short lifetime of the organic acids in the marine boundary layer, however, suggests that these were incorporated from the free troposphere and / or were locally produced. Chemical production of the organic acids, while ozone dependent, may have also been significant during high ozone days.

As of here, the local production and sink processes of HCOOH and CH₃COOH will be discussed separately in more detail.

Formic acid

In Table III-7 are estimates for the Sipaliwini area of some of the most important known chemical production pathways of HCOOH. All of the reactions are ozonolyses of naturally emitted alkenes or related species; of them, the most important is isoprene. The VMR data of the VOCs correspond to early afternoon airborne BL measurements in the area of Sipaliwini (Warneke, 1998; Warneke *et al.*, 2001). The ozone VMR (15 nmol mol⁻¹) is the average for the early afternoon. The sum of the reaction production terms in Table III-7 amounts to 28 pmol mol⁻¹ h⁻¹.

Precursor	VMR , nmol mol ^{_1}	Ozone VMR , nmol mol ¹	Rate k	Ref.	HCOOH Yield (c)	HCOOH pmol mol ⁻¹ h ⁻¹
Isoprene	2 - 4	15	1.28E-17	а	30%	20
Methacrolein	~1	15	1.33E-18	b	45%	1
MVK	~2	15	5.40E-18	b	45%	6
Ethene	~0.5	15	1.7 E-18	b	54%	1
					Net =	~ 28

Table III-7	Chemical	production	of HCOOH i	n Sipaliwini	durina I BA	A-CLAIRE
	Onernica	production	0110000111	n Olpanwin		

Reaction rates are for 298K, in molecule $\text{cm}^{-3} \text{ s}^{-1}$

Dry deposition rate is given as velocity, in cm s^{-1}

(a) Atkinson, 1994

(b) Atkinson, 1990

(C) P. Neeb, personal communication, 1999; also used by Von Kuhlmann (2001).

In-cloud aqueous phase oxidation of HCHO by HO radicals is a potentially important HCOOH production pathway; but pH dependent oxidation of the formate ion by HO radicals to CO_2 apparently reduces the net potential of cloud production significantly (Chameides and Davis, 1983; Chameides, 1984; Talbot *et al.*, 1990a; P.J.Crutzen, personal communication, 1999). For that reason, the contribution of HCOOH cloud production is ignored in this work.

The estimated velocity of deposition for HCOOH, of 1 cm s⁻¹ (Hartmann *et al.*, 1991), supposes an afternoon loss rate of 2.6% in the hour. A VMR of 1.25 nmol mol⁻¹, the afternoon average, would have implied an hourly loss of *ca.* 32 pmol mol⁻¹h⁻¹ by dry deposition. This cancels out with the estimated afternoon net chemical production rate of *ca.* 28 pmol mol⁻¹h⁻¹ in Table III-7. The average early afternoon VMR of HCOOH was constant, as shown in Figure III-15, and in fact its early afternoon variation on individual days was generally small. Similar calculations for days with high ozone and HCOOH levels (20 and 2.5 nmol mol⁻¹, respectively) lead to net loss of 10 to 30 pmol mol⁻¹h⁻¹ HCOOH. The resulting estimate of total afternoon loss is similar to the uncertainty of the data, so it cannot be verified.

The average morning increase rate of the HCOOH VMR (*ca.* 85 pmol mol⁻¹h⁻¹) would require very high concentrations of isoprene, in order to be the effect of chemical production alone. For an average morning ozone VMR of 13 nmol mol⁻¹ and an average HCOOH VMR of 0.8 nmol mol⁻¹, the required isoprene concentration is 22 nmol mol⁻¹, or else about 11 nmol mol⁻¹ each of isoprene, MVK and MACR. Such concentrations were not observed on any single day during the LBA-CLAIRE campaign.

Thus the morning increase of the HCOOH VMR must be explained as an effect of imports or of primary emission, or of a combination of both. The sources of HCOOH causing the morning increase are required to have become inactive in the afternoon hours, when Z_i was constant, just as well as the levels of organic acids. It is uncertain whether the local ecosystems stopped their emissions of HCOOH (if any took place) around midday, though it seems unlikely, according to Gabriel (1997), who found a direct relation between heat / insolation and direct emission of organic acids. It is certain that entrainment of free tropospheric air into the mixing layer ceased at or shortly after midday. So it seems more likely that the morning increase in the HCOOH levels was due to the entrainment of RL or FT air. These layers were constituted by air parcels advected into the continent, thus the HCOOH in the Sipaliwini area was apparently mainly imported.

Acetic acid.

Ozonolysis of isoprene does not produce acetic acid in any significant amounts (P. Neeb, personal communication, 1999). The known relevant chemical production pathways of CH₃COOH are reactions of acetylperoxy radicals with other peroxy radicals. Production of acetylperoxy radicals depends on radiation and availability of carbonyl compounds; the latter are produced during ozonolysis and during HO initiated oxidation of isoprene as well. Formation of CH₃COOH requires daylight. Unfortunately, an estimation of the VMR of acetylperoxy radicals in Sipaliwini has not been possible.

The only significant loss pathway of CH₃COOH in Sipaliwini was deposition; the available estimation of the velocity of deposition of CH₃COOH is 1 cm s⁻¹ (Hartmann *et al.*, 1991), equivalent to 2.6% in the hour. The approximately constant VMR of CH₃COOH during the afternoon hours suggests that the early afternoon production rate was similar to the loss rate by deposition of *ca*. 20 pmol mol⁻¹h⁻¹. However, the estimate of total loss by deposition during the afternoon and that of afternoon total production are similar to the uncertainty of the concentration data, so it is uncertain whether either or both took place.

The average morning increase rate of the CH₃COOH concentration was similar to that of HCOOH, around 85 pmol mol⁻¹h⁻¹. It is unlikely that chemical production could be responsible for this, because it would be required to cease shortly after midday, as in the case of HCOOH. As primary emission of CH₃COOH has no apparent reason to cease at midday either, it seems that the observed morning increase of CH₃COOH VMRs was an effect of the entrainment of RL or FT air, and consequently of imports. Furthermore, March 26 and 27, the days with strong subsidence in the region, had particularly high early morning levels of the organic acids: instead of the usual *ca*. 0.5 nmol mol⁻¹, they were closer to 1 nmol mol⁻¹.

III.3. Chapter conclusions

Consideration of the BL dynamics in the area under study has been key in the interpretation of the results of the various trace gas measurements. If the discussion of the BL dynamics is not in error, air from above the North Atlantic was advected every night over the nocturnal BL (NBL) in the area, apparently as far as Sipaliwini or beyond. This air constituted the residual layer (RL) and the free troposphere (FT) that were available next morning for entrainment into the mixing layer. The FT was probably constituted of fossil mixed layers that formed over the marine BL when a continental BL was advected over the ocean, whereas the RL was probably constituted of a mixture of air from the marine BL and air from the NBL upwind from the site.

The uncertainty of the CO data obtained at the sites precludes any conclusive evidence regarding the expected increases (Crutzen *et al.*, 1985; Williams *et al.*, 2001) with distance from the coast. What the ground based measurements did allow was an estimate of the day to day variability of the CO levels, which amounted to *ca.* 20 nmol mol⁻¹day⁻¹. The variation rate of the CO levels estimated from the ground data is similar to the expected (Crutzen *et al.*, 1985) and estimated (Williams *et al.*, 2001) increase rates; so the variation of the background CO levels should be considered when trying to assess the CO increase caused by oxidation of VOCs in the local BL.

The CO data at the coastal and inland sites showed the same day to day variation pattern; this is interpreted as an evidence of long range transport of the CO to the area, and it additionally supports the proposed nocturnal renewal of the RL and FT with air advected from above the North Atlantic ocean. Similar results for O_3 and the organic acids further support the above.

There was net loss of O_3 in the area, as inferred from the afternoon decrease in Sipaliwini and from the decreasing levels with distance from the coast. The ozone net loss rate was estimated from these two different informations, leading to similar results (*ca.* 5% in the hour). The net loss of O_3 considering reactions, deposition and in-cloud reaction was estimated to be between 4.2 % h⁻¹ and 7.7 % h⁻¹; this coincides fairly well with observations. The major organic acids found in the area were formic and acetic. This coincides with previous works. The diel cycle of these two acids in Sipaliwini suggests that a major source process was the entrainment of RL air, but mainly of FT air, taking place during the morning and early afternoon. Consideration of the other likely source processes, *v.g.* direct emission and production by reactions, leads to the same conclusion. That implies imports were the major source of these acids in the area, which is further supported by the observed day to day variation pattern and its coincidence with that of O_3 and CO.

Formic and acetic acids showed clear decrease in their concentrations for one or two hours after rain events. This affected HCOOH more strongly, as is to be expected from its larger solubility in water. The effect seems to imply an increased velocity of deposition for these two acids under wet conditions, and is therefore worth attention regarding measurements of dry deposition rates of these and other gases that have significative water solubility.

Several aspects of the observations point to imports as the determining factor for the levels of CO, O_3 and organic acids in the area. If that was the case, and NO_x levels were indeed as low as they apparently were, then the tropospheric chemistry up to Sipaliwini was essentially determined by the composition of the incoming air parcels, and upwind emissions had little effect on it. That was probably not the case further downwind from Sipaliwini, due to the expected NO_x emissions from the savanna area and the local biogenic NMHC emissions.

The choice of a remote pristine area with incoming air parcels from above the Atlantic ocean has shown that the air in such places is not necessarily also pristine, but rather carries the evidence of contamination taking place far away. That is possible because of the formation of a decoupled marine BL in continental boundary layers advected over the oceans, allowing for efficient transport of the gases and particles remaining in the air above that newly formed MBL, something that seems worth further consideration.

IV Compositional variation of rainwater in the Northeastern plains of Costa Rica.

IV.1. Basic considerations regarding the composition of rainwater.

Rainwater composition is determined by the composition of the air from and through which it precipitates. Air contains gaseous and particulate matter that can be uptaken or scavenged by water drops suspended in it or falling through it. Gases are taken up by water drops if they are soluble in water. Most atmospheric matter that is scavenged by rain originates directly or indirectly at the land or ocean surface; either as particles or as gases. An important part of gaseous emissions are naturally emitted hydrocarbons, mostly emitted by vegetation over the land surface. Many oxidation products of naturally emitted hydrocarbons, as well as some of the emitted substances themselves, are water soluble. In a region where marine air masses are advected into a continent, a change in composition of the air can be expected as it is transported inland. The composition of the air masses is changed by emissions occurring over land, by enhancement of convection and of associated rainfall, and by chemical reactions of the newly incorporated species. A gradual change in the character of the air mass from maritime to continental takes place as its contact time to the land surface lengthens. The consequent change in rainwater composition was the object of study of this work, with particular attention to organic acids, which are expected products of the oxidation of naturally emitted hydrocarbons coming from the vegetation on the land surface. Additionally, the sampling was carried out so as to observe variations in the rainwater composition within individual events.

IV.1.1. The scavenging action of clouds and rain.

Clouds and rain scavenge gas phase and particulate matter in the troposphere. For gas phase species, the mechanisms involved and the results differ according to their solubility and reactivity in water; for aerosols they differ according to particle size.

IV.1.1.1. Scavenging of gases.

Water soluble gases in a cloud are effectively taken up by the water droplets. These droplets can coalesce to eventually form raindrops, and raindrops can continue to scavenge soluble gases as they fall to the ground. This scavenging from the gas phase can be irreversible if the substance reacts chemically, as is the case of strong acids, which dissociate in water, and of ammonia, which reacts with hydronium ion to form ammonium. Or it can be reversible, if part of the substance does not react and has comparatively weak interactions with water, as is the case of most water soluble hydrocarbons and all volatile organic acids. The equilibrium state solubility of a gas in liquid water is described by the Henry distribution coefficient KH, equal to the concentration of the undissociated substance in the aqueous phase, divided by its partial pressure in the gas phase (this topic is discussed in most Physical Chemistry standard texts). Reversible uptake of a solute implies the possibility of loss of the solute from the droplet, e.g. when a droplet precipitates and the partial pressure of the solute in the air under the cloud is lower, when the droplet evaporates, or when the solute is displaced by some other solute being scavenged. Such is the case of the organic acids, when a strong acid like sulfuric or nitric, is taken up. The most important implication of reversible uptake is that it is limited to the equilibrium concentration, which can be displaced by changes in temperature and in composition.

The effectivity of irreversible scavenging of gases by falling droplets depends mainly on their size; smaller droplets are more effective. Variation of the diameter of a raindrop in one order of magnitude can imply variation of aqueous HNO₃ VMR over 2 orders of magnitude at the ground level, for example (Seinfeld and Pandis, 1998). For reversibly scavenged species in turn, the size of the raindrop determines how closely the equilibrium with the gas phase is approached. As a rule, fine rain is far more volume-effective at scavenging water soluble gases than large raindrops, and irreversibly scavenged gases.

Trace gases in the air parcels advected over the Northeastern plains of Costa Rica may have arrived by long range transport or were generated through local emissions and reactions.

IV.1.1.2. Scavenging of particulate matter.

Within a cloud, nucleation scavenging of aerosol is highly mass efficient; it incorporates most of the aerosol mass into the cloud droplets. Smaller particles are not as easily activated, and most in the submicrometer fraction remain as interstitial aerosol in clouds. Scavenging of remaining interstitial aerosol is comparatively slow, with lifetimes over 11 minutes for particles over 0.01 μ m in size. The lifetime of interstitial particles larger than ca. 0.03 μ m in size is longer than the typical lifetime of a cloud, of ca. 1 hour. Very small particles, due to Brownian movement, are more efficiently scavenged; for example, particles 2 nm in size have an estimated lifetime of ca. 24 seconds (Seinfeld and Pandis, 1998). As a result, if a cloud reevaporates before raining, even though the mass distribution remains essentially unchanged, the number distribution of aerosol changes drastically: the ultrafine size fraction is virtually eliminated. Thus aerosol originating by gas to particle conversion and forming fine and ultrafine particles can be efficiently scavenged by cloud droplets and incorporated to larger size fractions when the cloud reevaporates, mostly into the accumulation mode.

A cloud will rain if a significant number of droplets reach a precipitable size, around 1 mm. Small cloud droplets can grow by nucleation quickly to ca. 10 μ m in size, but subsequent growth by condensation is slow. Growth of cloud droplets beyond the tens of μ m occurs by collision and coalescence among them. Collisional efficiency is low for droplets below ca. 50 μ m in size. For a cloud to rain, about one droplet in a million must be ca. 100 μ m or larger in size; such cloud droplets have a large enough collisional efficiency to reach precipitation size before the cloud reevaporates (Seinfeld and Pandis, 1998); giant aerosol particles nucleate such large cloud droplets.

When clouds rain, the raindrops additionally scavenge particulate matter on their way to the ground. Under a raining cloud, particle scavenging efficiency of the falling raindrops increases slowly with decreasing particle size below ca. 0.2 μ m, and drastically with increasing particle size over ca. 1 μ m. The former obeys to Brownian diffusion, while the latter obeys to inertial impaction. The particle size fraction between 0.1 μ m and 1 μ m is often called the Greenfield gap, and its collection efficiency by falling raindrops 1 mm in size is about four orders of magnitude smaller than for particles 1.5 μ m in size (Seinfeld and

Pandis, 1998). Collection efficiency by falling raindrops increases for decreasing raindrop sizes. The scavenging efficiency for ultrafine particles and for particles larger than ca. 20 μ m is near 1, independently of the raindrop size. Scavenging rates of small raindrops are larger than those of larger raindrops; 1 mm rain can collect in the order of 100 times more particles if the drop size is ca. 0.2 mm instead of 2 mm (Seinfeld and Pandis, 1998).

Most of the mass of aerosol at remote sites is in the coarse size fraction; large proportions of smaller particles are associated to continental influence (Warneck, 1988; Seinfeld and Pandis, 1998). Very contaminated air frequently has comparable amounts of mass in the fine fraction and in the coarse fraction; sometimes the mass in the fine fraction is even larger in such air parcels; this effect is due to particles that originate in combustion processes. Marine aerosol is constituted essentially by seasalt, and usually shows some degree of enrichment of sulfate at the cost of equivalent depletion of anions forming volatile acid gases (anions as chloride, bicarbonate, bromide and so on). SO2 that is oxidized in the water film of aerosol particles or in cloud droplets has this effect. Sulfate enrichment factors in marine aerosol have been found to be in the order of 3.5 - molar ratio to Na+ increases from ca. 0.06 to ca. 0.21 - with respect to seasalt composition (Warneck, 1988; and references therein). SO2 in the marine boundary layer (MBL) is produced by oxidation of dimethyl sulfide (DMS) that is emitted from the ocean. Aerosol of continental origin contains important amounts of crustal and vegetal material, ammonium salts, and combustion related particles; the latter contribute very strongly to the fine and ultrafine size fractions, while the former contribute more to the coarse fraction. Continental aerosol is often poorer in larger size particles, as compared to marine aerosol, even though its total number concentration is usually much higher; as a consequence, marine aerosol is in general more effective at the nucleation of precipitable cloud droplets, hence of raining clouds (Seinfeld and Pandis, 1998).

Aerosols over the Northeastern plains of Costa Rica had sources as seasalt, local emissions and possibly long range transport.

IV.1.2. Other mechanisms affecting the composition of rainwater in the area.

Gases and particulate matter in the boundary layer undergo other loss mechanisms, apart from wet deposition. By affecting the air composition in the boundary layer, these mechanisms influence the rainwater composition indirectly. They are a consequence of the contact of the mixing layer to the water and the land surfaces.

IV.1.2.1.Dry deposition of gases and particles.

Dry deposition is one of the most important loss mechanisms for boundary layer particles and gases; it occurs essentially by collision of the gases or particles with surfaces. Dry deposition is greater over the land surface than over water surfaces. An air parcel being advected from above the ocean over the continent becomes depleted of the marine aerosol both by wet and by dry deposition. As is later discussed, the only form of deposition affecting the rainwater composition in the Northeastern plains of Costa Rica was dry deposition.

IV.1.2.2.Entrainment of air from the free troposphere.

Another mechanism influencing the composition of the mixing layer (ML) air, and therefore that of the rainwater falling from it, was the entrainment of air from the free troposphere (FT) over the Northeastern plains of Costa Rica. Entrainment of the FT takes place due to the incorporation of heat from the land surface, as explained in the previous chapter. The deepening of the mixing layer incorporates species available in higher concentrations in the FT and dilutes other ones. For example, it is well known that contaminants as dust and smoke are transported towards America above the marine boundary layer over the Atlantic ocean from the African and European continents (Prospero and Carlson, 1972; Raes, 1995; Raes et al., 1997; Li et al., 1996; Chiapello et al., 1997; Tyson and Dabreton, 1998; McDowell et al., 1990); entrainment of the FT makes these species available in the ML. Thus, entrainment of FT air was another factor affecting the composition of rainwater in the Northeastern plains of Costa Rica.

IV.2. A short background revision.

Precipitation has been studied at a variety of sites around the world, which can be grouped in types according to the surroundings and the major influences on the rainwater composition. A great deal of the sampling sites are urban or industrially influenced (e.g. Hermoso et al., 1990; Sempere et al., 1994; Beck, 1998; Almomani et al., 1995; Sakugawa, 1993; Kumar, 1993 and 1996; Kawamura, 1996a and 2001; Sequeira and Lai, 1998; Yu et al., 1998; Gulsoy et al., 1999; Patrinos, 1989; Whelpdale et al., 1997 and references therein) or rural (e.g. Ayers et al., 1995; Talbot et al., 1995; Chung et al., 1996; Granat et al., 1996; Sequeira et al., 1996; Khare, 1997; Almomani et al., 1998). Urban and industrially affected precipitation tends to show higher proportions of sulfate and nitrate than rural precipitation (e.g. Hermoso et al., 1990; Sanusi et al., 1996; Whelpdale et al., 1997; Gulsoy et al., 1999), which in turn shows high concentrations of ammonium and often also of organic anions (e.g. Sanusi et al., 1996; Whelpdale et al., 1997). However, several works have shown that the history of the air mass from which the precipitation falls is one of the strongest determining factors for its composition (Miller et al., 1980; Galloway et al., 1989; Chung et al., 1996;Yu et al., 1998; Pio et al., 1991).

More seldom, precipitation sampling works have been carried out in pristine environments as remote forests (e.g. Keene et al., 1983; Lacaux et al., 1987 and 1992a; Lance et al., 1991; Cautenet and Lefeivre, 1994; Granat et al., 1996; Williams et al., 1997), savannas (e.g. Sanhueza et al., 1987,1989 and 1992 ; Galy-Lacaux and Modi, 1998) and remote maritime areas (e.g. Galloway et al., 1989; Avery et al., 1991; Moody et al., 1991; Sempere et al., 1996; Koshy et al., 1997). Remote maritime precipitation tends to show the lowest concentrations of solutes other than seasalt, though influences from urban or industrial areas can lead to considerable variation (e.g. Miller et al., 1980; Galloway et al., 1989; Avery et al., 1991 and 2001). Most precipitation studies have been carried out in midlatitude areas. Studies of precipitation chemistry in the rainy tropics (between about 15° N and 15° S) are few, as compared to other regions of the world.

Unfortunately, many of the earlier studies and some recent ones have used techniques delivering data that are unreliable or difficult to interpret, as (wet-and-dry) bulk sample collection (e.g. Hendry et al., 1984; Alebic-Juretic, 1994; Báez et al., 1997; Cabon, 1999;

Taylor et al., 1999). Many works have employed sampling and / or analysis techniques excluding the organic acids and anions (e.g. Hendry et al., 1984; Eklund et al., 1997; Báez et al., 1997; Cabon, 1999; Taylor et al., 1999), even though these have shown to be an important part of the solutes, especially in remote areas of America and Australia (e.g. Keene et al., 1983; Galloway et al., 1982; Likens et al., 1987; Andreae et al., 1988b and 1990; Sanhueza et al., 1989 and 1992), but also in some industrially affected areas (Yu et al., 1998; Miyake et al., 2001). Most precipitation studies in the tropics involving organic anions have been carried out in the American hemisphere (e.g. Keene et al., 1983; Sanhueza et al., 1987,1989 and 1992; Andreae, 1987 and 1990; Lance et al., 1991; Williams, 1997). A few have been led in tropical Africa, mainly by Euro-African groups (Lacaux et al., 1987, 1992a and 1992b; Galy-Lacaux and Modi, 1998), and in tropical and subtropical Australasia by different groups (Likens, 1987; Koshy et al., 1995; Kumar et al., 1993; Khare et al., 1997).

The chemistry of precipitation in the rainy tropics varies somewhat, depending on the existing local influences and on the season. Dry season precipitation at any single location is usually more concentrated (e.g. Hendry et al., 1984; Eklund et al., 1997; Andreae et al., 1990; Lance et al., 1991; Williams et al., 1997). Wet season precipitation is more dilute, but deposes larger amounts of solutes (e.g. Hendry et al., 1984; Eklund et al., 1997; Andreae et al., 1990).

The Northeastern plains of Costa Rica were in 1996 still to a large extent rainforest, but have a strong maritime influence (Hendry et al., 1984; Eklund et al., 1997), being less than 200 km from the coast. The precipitation would be expected to show combined compositional characteristics of that of rainforest regions and of maritime areas.

The largest existing rainforest extension on Earth is the Amazon region. Rainwater in the central Amazon region has been found to be dilute and slightly affected by human activities (Williams et al., 1997, Galloway et al., 1982; Andreae et al., 1990); most of the solutes found in Amazon precipitation have been considered to be of local biogenic origin (Harriss et al., 1988, 1990). However, the ongoing massive deforestation and biomass burning in the Amazon region can easily inject large amounts of smoke and ash into the troposphere, also influencing the local precipitation chemistry (Williams et al., 1997; Harriss et al., 1988,

1990). Additional influences from long range transport of smoke and dust from Africa and Southern Europe (Talbot et al., 1990b and 1996; Artaxo et al., 1990; McDowell et al., 1990; Miller et al., 1980; Chiapello et al., 1997; Prospero and Carlson, 1972; Swap et al., 1992; Moulin et al., 1997a and b; Husar et al., 1997; Formenti et al., 2001) seem worth consideration. However, being the Central Amazon region over 500 km inland from the coast, a predominance of local sources of solutes in the precipitation should be expected.

Few studies of precipitation chemistry in tropical maritime areas - as islands or coastal siteswere found (McDowell et al., 1990; Miller et al., 1980; Koshy et al., 1997). The chemistry of precipitation in these areas is largely comparable to that of other maritime sites, such as Amsterdam Island (Galloway and Gaudry, 1984; Moody et al., 1991) and North Carolina (Avery et al., 1991) in that the two main influences seem to be the seasalt aerosol and long range transport of land related species - among them, anthropogenic contaminants. The studies by Hendry et al. (1984) and Eklund et al. (1997), as well as this work, show the precipitation of Northeastern Costa Rica to have a marked maritime influence. As later discussed, influences of long range transport and local processes also become apparent.

Precipitation studies including organic acids have become more frequent since the organic anions started to be found to be a significant part of the solutes in most areas of the world. Urban and industrially affected environments tend to show a larger variety of organic acids in precipitation, as well as relatively high concentrations (Kawamura and Kaplan, 1987; Kawamura et al., 1996a; Grosjean , 1989, 1992; Grosjean et al., 1994; Beck, 1998), apparently due mostly to combustion processes. However, a variety of dicarboxylic acids has been found in relatively high concentrations in rainwater samples from the Western Pacific ocean and related to long range transport of precursors from Australia and Asia (Sempere and Kawamura, 1996a). Non maritime remote sites often show somewhat higher proportions of organic acids in relation to total solutes (Khare et al., 1999, and references therein). Of the precipitation studies led at remote sites in Costa Rica, only this work has included organic acids; as discussed later on, there is better comparability of the results to maritime than to forested areas.

IV.3. The sampling work in the Northeastern plains of Costa Rica.

Rainwater was sampled at several sites in the northeastern plains of Costa Rica from July 8 to July 29, 1996. Figure IV-1 shows the location of the sampling sites; they were located along an almost straight line approximately following the expected wind direction during the period. Distance from the coast along the average wind direction (E-NE) will be referred to throughout this chapter plainly as distance from the coast; it was 1 km at Tortuguero (10°38'N, 83°32'W; sea level), ca. 60 km at Las Ahogadas (10°32'N, 84°02'W; 20 m asl) and La Selva (10°25'N, 84°00'W; 35 m asl), and ca. 80 km at Veracruz (10°31'N, 84°15'W; 80 m asl). Samples were also collected at an intermediate site between Tortuguero and Las Ahogadas, about 20 km from the coast; unfortunately, those data had to be eliminated because of apparent contamination with dust from a nearby street. All sampling sites were below 100 m asl, as well as their surroundings in a radius of 5 km or more.

All rain events were sampled, day and night, with the exception of events shorter than 5 minutes and of events smaller than *ca*. 0.1 mm. Sampling was manual, using bottle and funnel; electronic alarms were used at night time to warn for starting rain events. The sampling procedure has been described in detail in the experimental part (Chapter I), as well as all preservation and conservation measures employed. Rain events were sampled in fractions according to elapsed time (usually a sample after 10, 20, 30, 60, 180 and 300 minutes). A rain event was defined as ended after 15 minutes without rain and the last fraction was collected at that moment. The samples were analyzed posteriorly for anions, cations and pH. The major cations analyzed were Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺. The main anions found in the samples were Cl⁻, NO₃⁻, SO₄^{2⁻}, formate, acetate, oxalate and propionate. The analytical details are given in the experimental part (Chapter I).

The Biological Station La Selva, in charge of the Organization for Tropical Studies (OTS), was the operations headquarters as well as a sampling site. At the sampling sites Tortuguero and La Selva, the samplers were located 50 to 100 m from a forest canopy, while at the other sites the forest canopy was at least 500 m away and grass predominated several kilometers around. A meteorological station was set up near the site Las Ahogadas, on the top of a small treeless hill. Additionally, daily average temperature and precipitation data were provided by the OTS from a meteorological station operating at La Selva station.



Figure IV-1. Location of the rainwater sampling sites in the northeastern plains of Costa Rica. Between the sites and the coast there was mostly forest and pasture. T = Tortuguero; LA = Las Ahogadas; LS = La Selva; V = Veracruz.

IV.4.Results and discussion.

Before presenting results, it is worthwhile to point out one of the limitations of this work. Because of the shortness of the sampling period (three weeks, one dry and two rainy), total deposition of solutes is only briefly addressed here. The relatively low frequency of rain events at any given site causes the total volume of precipitation at that site to be highly variable in short time spans (shorter than one or two weeks, for rainy areas). High variability in volume leads to high variability in deposition of solutes. Sampling periods of a few months or years are more adequate for total deposition studies.

IV.4.1. Meteorological aspects and ozone levels.

IV.4.1.1.Wind and transport.

Wind direction during the period was in average NE, with surface speeds between 1.5 and 3 ms⁻¹ about 15 m above ground level from 10:00 to 18:00 LST. Direct measurements of the wind speed in the rest of the mixing layer are not available. As a rule, wind speed in the daytime boundary layer approaches zero near the ground and increases more or less logarithmically with height, until reaching a fairly constant value above 100 to 200 m above the ground (Stull, 1988). Cloud (shadow) displacement speed at different sites was estimated on three different days; estimates were 4, 5 and 7 ms⁻¹ with 20% uncertainty; the average was (5.3 ± 1.1) ms⁻¹. A mean mixing layer wind speed over the area of about 5 ms⁻¹ is estimated from here for the sampling period. No calms occurred at daytime during the sampling period. After 17:00 LST surface wind speed tended to decrease and to approach zero.

Surface sea-to-land breeze (at daytime) had the same direction as the synoptic scale wind (Trades). It is improbable that a circulation cell along the coast could build up during the day, because the wind speed in the area was high enough to obliterate this effect (Garratt, 1992). Nocturnal land-to-sea breeze can represent a local transport factor towards the ocean for gases and aerosols originating over land. Likely outward breeze did not have a net effect at Las Ahogadas, 60 km inland from the coast, where the meteorological station was installed. However, a narrower cell (< 60 km) may have built up along the coast at night; such a cell could favor night time and morning rains at the coast, but would be of
little consequence for the air composition in the area during most of the daytime. So transport was essentially from E-NE in the area, at a speed of *ca*. 5 ms⁻¹ in most of the BL, until July 28, when a low pressure system North of the area (hurricane Cesar) led to a change in the wind direction, as below discussed.

Ten day back trajectory plots for the area at arrival altitudes of 500 m, 1000 m and 2000 m asl were made available by NOAA's Climate Monitoring and Diagnostics Laboratory, using the method of Harris and Kahl (1994). These show that the air parcels arriving in the sampling area possibly came mainly from above the North Atlantic near northwestern Africa and southwestern Europe, and from the South American subcontinent after July 27. Table IV-1 shows the information for the sampling period; related plots are to be seen in Appendix 4.

Dates in July 1996	Starting area (on day -9)	Subsidence
10 - 13	North Atlantic, near NW Africa and SW Europe	very weak
14 - 15	Transition	
16 - 18	Central Amazon, continuing over Venezuela / Colombia.	weak
19	Transition	
20 - 26	North Atlantic, near NW Africa and SW Europe tending to equatorial Atlantic, near NW Africa	weak
27 - 28	North Atlantic, near the Azores	regular
29	Pacific Ocean and western South America, Peruvian coast	weak

Table IV-1 Transport of air parcels to the sampling area according to ten day back trajectory calculations.

Representative plots to be seen in Appendix 4.

Before July 28, the sampling area was subject to advection of the Atlantic marine boundary layer (MBL) over it. Advection of a marine air mass over the land surface has a variety of implications for the dynamics and composition of the advected air mass. The boundary layer (BL) at Tortuguero (the coast) is marine, with depth values (Z_i) typically around 600 to 700 m. Uptake of particulate matter coming from the soil and the vegetation, as well as

of emitted gases, must have effected gradual compositional changes in the advected air masses; meanwhile, dry deposition of components with smaller or no source processes over land must have caused depletion of these components. An important effect of the advection of this humid MBL over land is that turbulence in it increases because of warming by the land surface; and therefore Z_i must also increase over land. Deepening of the convective boundary layer implies entrainment of free tropospheric air, which has a different composition. The air being transported above the MBL to the sampling area may have contained materials such as dust, smoke and industrial contaminants, according to where it had been part of the boundary layer before. Increasing convection of humid air masses leads to increased cloud formation. In the clouds, processes with an influence on the air composition take place, as rainout and cloud processing of aerosols and aqueous phase chemical reactions involving newly incorporated species. Wet deposition was probably not an important factor differentiating the BL composition at the different sites during this work, as is later discussed, except during the stratocumulus rains and drizzles occurring after July 27.

IV.4.1.2.Rainfall and temperature

During the first days of the month, rainfall was not as regular as other years in July, but became more regular after July 15. The overall average afternoon (12:00 to 17:00 LST) temperature recorded at La Selva in July 1996 was 28.9° C (sd = 1.8° C, from hourly means) and the overall night (22:00 to 5:00 LST) average 23.2° C (sd = 0.7° C, from hourly means) (personal communication, T. Brenes, OTS, 1998). During the sampling period, the warmer days had the least rainfall; this was before July 15. Figure IV-2 shows afternoon temperature means and daily rainfall volume during July 1996 at the biological station La Selva. Afternoon temperatures responded mainly to insolation, and the greatest contrast during the period was between the days before July 15, with hardly any clouds, and those after July 26, with overcast skies most of the time, which led to somewhat lower temperatures in the daytime.

After July 27, the region was affected by a hurricane which was passing some 400 km to the North of the sampling area. Populations on the Caribbean coast were evacuated starting on July 26; the persons in charge of the coastal sampling site were evacuated on July 27. The

northeastern plains of Costa Rica were covered in those days by a thick layer of clouds; light rain and drizzle dominated from then on, especially on July 28. As it turned out, the Atlantic region of the country was affected only by light stratocumulus rains, while the Pacific side was subject to desastrous floods and loss of houses, roads, bridges and several lives. The sampling work ended early on July 29.

Rainfall amounts.

Rainfall occurred mainly under three sets of conditions: a) dry days with much sun, very few clouds and occasional short showers from cumuli (July 8-15); b) cloudy days with some sun and more frequent showers or storms (most days from July 15 to 26) and c) overcast days with much drizzle and occasional more intensive rain, mostly from stratocumulus clouds (after July 26). In Table IV-2, the days during the sampling period have been grouped according to rainfall conditions in the area.



Figure IV-2. Rainfall and afternoon average temperature (12:00 to 17:00 LST) at La Selva during July 1996.

Figure IV-3 shows the daily rain volumes at three representative sites. As seen there, few days had comparable rainfall volumes at all three sites. However, total amounts recorded for the sampling period (Table IV-3) were similar at three of the sites and *ca*. 50% larger at La Selva. The larger amounts of precipitation at La Selva may have been due to orographic effects, since the station is located at the southern side of the plains, near the mountains southwest from it; however, the sampling period is too short to exclude plain natural variability as the cause.

Conditions	Number of Days	Dates
Isolated showers or storms	7	10, 12, 14, 17, 18, 19 and 25 July
Rainy overall	9	15, 20, 21, 22, 23, 24, 27, 28 and 29 July
Dry	6	8, 9, 11, 13, 16 and 26 July

Table IV-2. Conditions regarding rainfall during the sampling period.



Figure IV-3. Rainfall at three sampling sites in the northeastern plains of Costa Rica during July 1996. Tortuguero had no sampling during the last two days shown, due to the hurricane alarm.

	$L m^2 day^{-1} *$	$L m^{-2}$ (total) *	dates/days
Tortuguero	16	194 (243**)	July 15-26 / 12
Las Ahogadas	13	199	July 15-29 / 15
La Selva	24	357	July 15-29 / 15
Veracruz	16	240	July 15-29 / <i>15</i>

Table IV-3. Total rainfall at the sampling sites from July 15 to the end of the sampling period.

*Uncertainty of rainfall volume measurements was 10%. ** Extrapolation to 15 days (the sampling had to be interrupted two days earlier at the coastal site due to hurricane alarm).

IV.4.1.3. Ozone levels

The ozone gas phase volume mixing ratio (VMR) was measured at La Selva; data are available for most of the days in the sampling period. As explained in the experimental part (chapter I), the air inlet was *ca*. 6m above the ground. The overall mean for afternoon hours was 11 nmol mol⁻¹, with a minimum of 5 nmol mol⁻¹ and a maximum of 20 nmol mol⁻¹ during the sampling period. The mean diel cycle is shown in Figure IV-4; as seen there, the values started to rise during the morning usually after 8:00 LST and fell in the afternoon after 16:00 or 17:00 LST. In contrast to the diel cycle seen for Sipaliwini (Chapter II), where the nighttime and afternoon data had the lowest dispersion, the dispersions of all daytime data in Costa Rica are very large. This was partly due to day to day variability, but also to relatively high variability within single days.

An aspect of this variability is seen in Figure IV-5; the afternoon means for July 20 and 26 are very similar, but the diel cycle was quite different on these two days. Note that on July 20 there was relatively strong variation during the afternoon, while July 26 presented a quite flat afternoon.



Figure IV-4. Hourly mean values for O_3 concentrations during the sampling period. Error bars are 1 standard deviation of hourly means.



Figure IV-5. Ozone diel cycle on two days during the sampling period, recorded at La Selva. Hourly means. Different degrees of variability occurred in the afternoon.

In general, nocturnal values were near zero, similar to that observed in other forested sites (Fan *et al.*, 1990; Quesada *et al.*, 2000); this is attributable to fast depletion of O_3 in the lower levels of the newly established NBL. Daytime ozone levels at a coastal site with incoming trades would be expected to show little variation during the afternoon, as seen in Costa Rica on July 26 and as observed in 1998 at Petit Saut, French Guiana, by C. Galy-Lacaux and D. Serca (personal communication, 1999). The air arriving at La Selva from the Caribbean had passed the coast 3 to 4 hours before, considering the wind speed observed during the sampling period, so all air during the afternoon had the same time of contact to the land surface. Variability occurring during the afternoons probably reflected that of the ozone content in the incoming air parcels.

The day to day variation during the period is shown in Figure IV-6. Afternoon means are used; the reason to consider only afternoon values is that these represent the concentration in the fully developed mixing layer, and is well explained in Chapter II. The overall mean was 11 nmol mol⁻¹, with a minimum of 5 nmol mol⁻¹ and a maximum of 20 nmol mol⁻¹.



Figure IV-6. Ozone afternoon average concentrations measured at the site La Selva during July 1996. Data from 11:00 to 16:00 LST were used to obtain the averages. Error bars are 1 sd, and reflect the variability during the afternoon. Data for July 24 and 25 are not available.

The values seen in Costa Rica are somewhat lower than those observed during July in Barbados (*ca.* 15 nmol mol⁻¹), a marine site, and at the lower end of that seen in other tropical North American sites during the rainy season, between 13 and 17 nmol mol⁻¹ (Sanhueza *et al.*, 2000). The location of the ozone measurements was relatively near to the coast (60 km), so a large difference with respect to maritime air O₃ levels is not to be expected. Fan *et al.* (1990) reported average daytime deposition velocities near 1.8 cms⁻¹ in the central Amazon during the rainy season. With such a high deposition rate and an average mixing layer height (Z_i) of 800 m between the coast and La Selva, the loss by deposition would be near 25% of the original MBL concentration at the coast, this is, about 3.5 nmol mol⁻¹. Additional losses by reaction are possible, so the original levels at the coast under these conditions might have been near 15 nmol mol⁻¹, similar to observations at Barbados.

The variations seen in Figure IV-6 were probably due to different O_3 contents in the air parcels advected into Costa Rica. The largest of these variations are the transition from July 14 to July 16 and the drop after July 27. Table IV-1 shows July 14 and 15 as transition days between transport from the Northwest African or Southwest European region and transport from the Central Amazon region.

Northwestern Africa is a frequent source area of Saharan and Sahelian dust, especially in the summertime, and of smoke (*e.g.* Chiapello *et al.*, 1997 and references therein), thus of ozone precursors. Southwestern Europe during the summertime is a likely important contributor of ozone precursors. This may explain the high O_3 values recorded on July 14 and the subsequent decrease with changing origin of the air parcels.

July 29 appears in Table IV-1 as having transport from the low troposphere in the equatorial American Pacific region. The drop in the ozone values approximately coinciding with the trajectories originating near the Pacific South American coastline agrees with low levels expected from this region.

The Amazon region is a potentially important source of smoke during the local dry season, due to biomass burning (Andreae *et al.*, 1988b). July is early dry season in the Central Amazon (Harriss *et al.*, 1988). However, similarly low values were recorded in air parcels advected from the Central Amazon region and from the Azores (North Atlantic) area.

IV.4.2. The composition of the rainwater at the sites.

IV.4.2.1. General aspects

Several general aspects are worth pointing out before going into more detail in the description of the rainwater composition at the sites. The main interest of this work are the carboxylic acids found in the samples. Organic acids found in the samples include, in order of usual abundance, formic, acetic, oxalic, propionic, lactic or its 3-hydroxy isomer, pyruvic, and perhaps malonic acids. While formic and acetic acids were consistently quantified in this work, oxalic and propionic acids were only occasionally quantifiable. As to lactic acid and its isomer, their retention time coincided with an artifact from the sampling materials (explained in the experimental part Chapter I), and are not further discussed. The rest of the carboxylates were usually below the limit of detection (LOD), therefore not quantifiable, even though often detectable. Note that the LOD, according to the definition used in this work (see section II.1.5), is the lower size limit for quantifiability of an existing (visible) signal.

Rainwater samples collected during the dry days were often more concentrated than those from the rainier period, after July 14. Unfortunately, samples from the dry period are too few to make any comparisons among sites.

Total wet deposition (in rain, in this case) of the analyzed solutes was higher when more precipitation occurred, furthermore, when higher precipitation rates occurred (see Table IV-4). As a result, events with higher precipitation rates often had also higher deposition rates of solutes and produced larger total deposition of solutes, even though frequently at lower concentrations. As an example, at La Selva an event of 1.2 mm on July 9, the only one on that day, deposed 19 μ mol m⁻² formate at a maximum rate of 1.6 μ mol m⁻² min⁻¹, whereas the larger event of July 24 (62 mm) deposed over 240 μ mol m⁻² formate at a maximum rate of 5.4 μ mol m⁻² min⁻¹. The mean concentration of the smaller event was much higher: 15 μ M formate against 4 μ M for the larger event. Table IV-4 illustrates this with three example events. Higher deposition rates coinciding with higher precipitation rates have previously been reported by a number of other workers, among them Hendry *et al.*, (1984), Báez *et al.* (1997), Andreae *et al.* (1990) and Lance *et al.* (1991).

Within events, precipitation rate and deposition rate maxima often coincided (the sampling procedure resolved fractions of the events), as is later discussed in this chapter.

DATE	Mean R _P (mm min ^{−1})	VW mean concentration (µM)	Mean / Max. R_{D}^{*} (µmol m ⁻² min ⁻¹)	Total time / Total volume (min / mm)	Total deposition (µmol m ⁻²)
09.07.96	0.06	15	0.9 / 1.6	21 / 1.2	19
22.07.96	0.8	3.1	2.5 / 3.2	64 / 53	160
23.07.96	0.6	3.0	1.8 / 6.1	122 / 68	220
24.07.96	0.2	3.9	0.8 / 5.4	282 / 62	245
RP = preci	pitation rate;	RD = deposition ra	ite; VW = volume we	eighted; * maintai	ined for 15 min.

Table IV-4. Characterization of three large events from the rainy period and one short event from the dry period at La Selva. Formate content is used as the example.

IV.4.2.2.Site specific volume weighted average concentrations (VWAC).

In this section, site specific average composition of the rainwater is presented and compared among the sites. The solute species are grouped according to expected or apparent sources and according to behavior with distance from the coast as: a) solutes related to marine aerosol, b) carboxylic acids and c) other species related to processes occurring over land. Marine aerosol was expected to be the main source of NaCl, sulfate and magnesium. Hydronium was grouped with the carboxylic acids, because these were expected to be its major sources at the inland sites. The last group includes potassium, calcium, nitrate, and ammonium, all species expected to have sources over land and actually showing concentration increase with distance from the coast.

In order to summarize the information on the analyzed rainwater components at the different sites, volume weighted average concentrations (VWAC) were obtained from the individual sample data. In calculating a VWAC, weight is given to the concentration data according to the volume of rainwater having that concentration. VWAC is given by

VWAC = Σ (Concentration_i * Rain Volume_i) / Σ Rain Volume_i,

where *i* identifies the time during which the sample was collected – fractionation of the events was made according to time, not to volume (experimental part). The VWAC is equivalent to the concentration that the total of the sampled rainwater would have had, had it been mixed. A plain averaging procedure gives equal weight to all concentration data, regardless of the volume they represent, being therefore a poor alternative. The VWACs in this section cover the sampling period from July 14 to July 29, and are specific to the sites. The VWACs in this work have an uncertainty of *ca*. 17%, which is mostly due to that of the rainfall volume.

Components related to seasalt

As the area under study is near the coastline, seasalt aerosol constitutes an important part of the solutes in the rainwater samples. Sea water has a notably constant composition, near the marine surface, all around the world (Seinfeld and Pandis, 1998; R. Jaenicke, in Hobbs, 1993). The major solutes in surface seawater are listed in Table IV-5. The species listed in Table IV-5 comprise over 99% of the mass of solutes in seawater.

Species	M (g/mol)	% m/m	mol X / mol Na
Cl-	35.45	55.04	1.166
Na+	22.99	30.61	1.000
SO42	96.06	7.68	0.0600
Mg2+	24.31	3.69	0.1140
Ca2+	40.08	1.16	0.0217
K+	39.09	1.1	0.021
	Sum:	99.3 %	

Table IV-5. Major seasalt components and molar ratios in reference to Na.

(Composition data from Seinfeld and Pandis, (1997))

The fraction of the solutes corresponding to seasalt is customarily obtained by reference to the Na⁺ content –under the assumption that all Na⁺ comes from seasalt–, because sodium is a major component in seawater and there are usually no other significant sources of this element in most places. The formula used is

$$[X_{nss}] = [X_{sample}] - [Na_{sample}] * ([X_{marine}] / [Na_{marine}])$$

where X stands for the solute species of interest. Table IV-6 shows the nss fractions for the species listed in Table IV-5, for each of the sampling sites in this work. The uncertainty for the nss fractions is near 20% of the total VWAC, as shown for Cl⁻ and Na⁺. It is seen in Table IV-6 that the nss fractions of Cl⁻ and Mg²⁺ are not significant, while smaller than the uncertainty of *ca*. 20% of the total. Therefore, Na⁺, Cl⁻ and Mg²⁺ most likely had seasalt as their only source. In contrast, SO₄²⁻, Ca²⁺ and K⁺ did have significant nss fractions. About 50% of SO₄²⁻ was non seasalt at all sites, while most Ca²⁺ and K⁺ were non seasalt. The decrease of Ca²⁺ and K⁺ with distance from the coast is discussed further on in this section.

The major seasalt (**ss**) solutes' site specific VWAC are shown in Table IV-7 with their corresponding uncertainties; ss sulfate is included. The VWAC values of all four components decreased with distance from the coast, as shown in Figure IV-7. While Na⁺, Cl⁻ and Mg²⁺ and ss SO₄²⁻ show a decrease rate of *ca*. 0.4% km⁻¹ (Table IV-7), total SO₄²⁻ shows a decrease rate of about 0.2% km⁻¹. However, neither total nor non seasalt SO₄²⁻ VWAC differed significantly from site to site; the uncertainty of the data is larger than the differences.

Depletion of seasalt from the air parcels entering the continent is a consequence of dry and wet deposition. Within the short distance from the coast covered by the sampling work (*ca.* 80 km), it is likely that an air parcel generated rain at most once. So the main deposition mechanism behind the decrease in the concentrations of seasalt ions must have been dry deposition. The scavenging efficiency of rain for seasalt particles probably varied little with distance from the coast, so a loss rate for the particles in the air parcels can be inferred from the variation of concentration in the rainwater samples with distance from the coast and the mean wind speed. The rate of depletion for seasalt aerosol between the Atlantic coast of South America and the central Amazon basin during the rainy season, of about 7% h^{-1} to 13% h^{-1} (Andreae *et al.*, 1990). There, loss processes did include wet deposition, due to longer transport times from the coast to the inland sites.

	Na⁺	Na⁺	CI	сг_	CI_	Mg ²⁺	Mg ²⁺	Mg ²⁺	SO4 ^{2⁻}	SO4 ^{2⁻}	SO4 ^{2⁻}	Ca ²⁺	Ca ²⁺	Ca ²⁺	K⁺	K⁺	K⁺
SITE	total	nss	total	nss	%nss	total	nss	%nss	total	nss	%nss	total	nss	%nss	total	nss	%nss
Tortuguero	31.9	0	31±5.2	-6.4±7.6	-21%	3.6	-0.04	-1%	3.3	1.4	42%	1.8	1.1	61%	2.3	1.6	71%
Las Ahogadas	15.9	0	20±3.3	1.2±4.5	6%	2.2	0.39	18%	2.7	1.8	65%	1.8	1.5	81%	2.5	2.2	87%
La Selva	23.8	0	22±3.4	-5.5±5.2	-24%	2.8	0.09	3%	3.1	1.7	54%	2.1	1.6	75%	3	2.5	83%
Veracruz	20.4	0	22±4.4	-2.3±5.9	-11%	2.5	0.17	7%	2.8	1.6	56%	4.3	3.9	90%	3.6	3.2	88%

Table IV-6. Total and non seasalt VWA concentrations (µM) of seasalt related components at the sampling sites.

Concentrations are expressed in µM; site specific VWM values are used. **Uncertainties** of the calculated nss fractions are slightly larger than those of the total VWM, which are *ca.* 20% of the total VWM (shown for Cl⁻). "%nss" is relative to the total VWM.

SITE	Na⁺	±	Cl	±	Mg ²⁺	±	SO4 ^{2⁻} (ss)	±	SO4 ^{2⁻}	±
Tortuguero	32	5	31	5	3.6	0.6	1.9	0.8	3.3	0.7
Las Ahogadas	16	2	20	3	2.2	0.7	1.0	0.7	2.7	0.6
La Selva	24	3	22	3	2.8	0.5	1.4	0.8	3.1	0.6
Veracruz	20	3	22	4	2.5	0.6	1.2	0.7	2.8	0.5
loss rate (km^{-1})	0.15 µM =	0.45%	0.13 µM =	0.4%	0.015 µM =	0.4%	0.006 µM =	0.45%	0.006 µM =	0.2%

Table IV-7. Total and ss VWA concentrations (µM) with uncertainties for the major seasalt components at the sampling sites



Figure IV-7. VWAC of seasalt components in rainwater at four representative sites. Lines and slope were calculated by the least squares method. Error bars represent the uncertainty. Lower values at 60 km correspond to Las Ahogadas.

Carboxylates and hydronium.

Table IV-8 shows the site specific VWACs of carboxylates and hydronium. H^+ has been grouped with the organic acids because, in tropical vegetated environments of America, formic and acetic acids are frequently major sources of H^+ (*e.g.* Galloway *et al.*, 1982; Andreae *et al.*, 1988b and 1990; Sanhueza *et al.*, 1987, 1989 and 1992;). In fact, hydronium was strongly correlated with the concentrations of formate and acetate in the rainwater samples, especially inland – discussed in more detail in the next section of this chapter. The most abundant organic acids were formic and acetic; oxalate and propionate were found in much smaller concentrations, and other organic acids as pyruvic and glyoxylic were usually below the limit of detection (LOD).

As seen in Table IV-8, oxalate VWAC values are smaller at all sites than their uncertainty; the concentrations in the samples were most often below the LOD, and when above, they were always very near to it. Comparatively, more samples from Veracruz contained oxalate concentrations larger than the LOD. So, even though a quantitative differentiation of the sites is not possible with the present data set, the samples from Veracruz clearly had higher contents of oxalate relative to the coastal site. The same holds for propionate, not shown in the table. Formate represented 3% to 4% of the total quantified ionic equivalents at all sites, whereas acetate amounted to 2%.

SITE	Ox	±	Ac	±	For	±	H⁺	±
Tortuguero	0.1	0.3	1.5	0.4	2.8	0.4	4.6	1.5
Las Ahogada	is 0.1	0.4	1.8	0.3	3.3	0.5	9.6	2.3
La Selva	0.1	0.3	2.2	0.4	4.0	0.6	6.9	1.7
Veracruz	0.3	0.3	1.6	0.4	2.7	0.4	3.1	1.0
	Ox = oxalate,	Ac = ac	etate, Fo	r = formate	e, H⁺ = nc	n-CO ₂ hyc	Ironium	

Table IV-8. Site specific VWAC of the major carboxylates and hydronium ion contained in the rainwater samples from Costa Rica. Concentrations in µM.

Differences in formate and acetate concentrations from site to site were mostly smaller than the uncertainty of the VWAC, and did not follow a clear trend. An increase tendency in the

VWAC with distance from the coast is not clearly seen. Hydronium ion concentrations also did not show a clear trend with distance from the coast (Table IV-8); the value at La Selva was higher than at the coast, but at Veracruz it was lower. All the H⁺ VWA pH values are relatively high, above 5. The hydronium value at Las Ahogadas, due to its large uncertainty, was comparable to that of La Selva. At all sites except La Selva, the sum of HCOOH and CH₃COOH VWAC is similar to the H⁺ value. Veracruz was the only site with a H⁺ value lower than the sum of the HCOOH and CH₃COOH values. The lower H⁺ level in the Veracruz samples is apparently related to the presence of a neutralizing agent occurring in the samples; this is further discussed later on in this section in relation to calcium content and to the HCOOH/CH₃COOH ratio.

The relative abundance of formate and acetate (about 4% and 2%, respectively) in the rainwater at the different sites was significantly lower than that observed at other inland remote areas, as the Venezuelan savannas (Sanhueza *et al.*, 1992), the Mayombe forest (Lacaux *et al.*, 1992a) and the central Amazon (Williams *et al.*, 1997), where together they usually amount to more than 20% of the total ionic equivalents. The large proportion of seasalt components in the Costa Rica samples is the reason for this. However, the contents measured in this work are also lower than those in the mentioned works and in other ones at similar sites. The concentrations of formate and acetate were similar to those found in the central Amazon during the rainy season (Andreae *et al.*, 1990) and on Amsterdam Island (Moody *et al.*, 1991; Galloway and Gaudry, 1984).

Hereafter in this section, the central issue is the variation of the VWAC of the organic acids with distance from the coast. Their major supply and losses are roughly estimated in order to explain the observed results.

The mixing layer in the area was, during most of the day, a marine BL being advected over land. Z_i was not measured in this work; but a safe estimate can be made: the marine BL in tropical latitudes is normally 600 to 700 m (Stull, 1988). This is valid for the coast; the other sites had a deeper mixing layer (ML), which can also be estimated by assuming an increase rate of Z_i similar to that seen in Surinam during the LBA-CLAIRE campaign. This was *ca*. 35 m for every 10 km (from afternoon data; see previous chapter, Table II-2). The increase rate in Costa Rica was probably similar, amounting to *ca*. 300 m in 80 km, the distance of the innermost site from the coast. So, in Veracruz, the ML had been over land about 4.5 hours, and was probably around 1000 m thick in the late morning and early afternoon.

As discussed in the corresponding section of the LBA-CLAIRE chapter, the main factors possibly affecting the organic acids levels in these tropical forest environments were primary emission, local production and deposition processes. All these had about 4.5 hours to affect the incoming air in the area under study.

Dry and wet deposition were the most important loss processes for the organic acids in the ML over land, the same as in Surinam during LBA-CLAIRE. An estimate of the dry deposition rate of HCOOH and CH₃COOH can be made from their velocity of deposition (V_d), their concentrations and the thickness of the mixing layer Z_i . V_d for these organic acids has been estimated in *ca*. 1 cm s⁻¹ in previous works for savanna/forest areas (Hartmann *et al.*,1991; Sanhueza *et al.*, 1992).

The levels of these organic acids in the marine BL are usually not higher than 500 pmol mol¹. As for Z_i , 800 m is a likely average for the sampling area. From these values, the loss by dry deposition may have been in the order of magnitude of

$$\{1 \text{ cms}^{-1} / (800 \text{ m})\} \bullet 0.5 \text{ nmol mol}^{-1} \approx 20 \text{ pmol mol}^{-1} \text{ h}^{-1}.$$

A daily dry deposition rate can be estimated from here, taking into account that about 9 out of 10 hours it did not rain, and making the rough assumption that dry deposition was possible at that rate for 12 hours in the day. From there, the dry deposition may have been similar to 10 μ mol m⁻² day⁻¹.

Wet deposition quite variable from day to day and from event to event. Very large rain events deposed as much as 200 μ mol m⁻² formate, as shown in Table IV-4, while a small event in the dry period deposed around 20 μ mol m⁻² formate. Average daily wet deposition rates during the rainy period were **45** μ mol m⁻² day⁻¹ for HCOOH and **25** μ mol m⁻² day⁻¹ for CH₃COOH, except at La Selva, where they were about twice as large. According to this, the wet deposition rate in the area was several times as large as the estimated average dry deposition rate. The average total daily deposition rate in the area was probably around 55 μ mol m⁻² day⁻¹ for CH₃COOH.

As previously mentioned, an air parcel probably underwent precipitation (rain) at most once during its advection over the sampling area. Thus, the only deposition process affecting the air mass, before it rained over any one of the sites, was dry deposition. So wet deposition had no effect on the VWAC of solutes in the rainwater samples collected at each site.

Processes that may have supplied HCOOH and CH₃COOH to the ML in the area were primary emission, production by reactions, and incorporation from the FT. It seems clear that a background concentration of HCOOH and CH₃COOH existed in the MBL, evidenced by the concentrations in the samples from the coastal site. Primary emission apparently did not play an important role in Sipaliwini, as discussed in the previous chapter; it was probably the same case in Costa Rica. As for local production by reactions, the only available information regarding precursors is the O₃ mixing ratio, which was slightly lower than in Sipaliwini, during the LBA-CLAIRE campaign. The VMR of reactive hydrocarbons that are precursors of HCOOH were probably similar or lower than in Sipaliwini. So a similar or lower chemical production rate than in Sipaliwini, v.g.. about 30 pmol mol⁻¹ h⁻¹, can be reasonably assumed. The production rate of CH₃COOH was likely in the same order of magnitude.

It is likely that entrainment of air from the layer above the MBL, here considered as the FT, significantly contributed to the gas phase mixing ratios of the organic acids at the inland sites, as it apparently was the case in Surinam. The lower part of the FT probably had higher levels of organic acids than the marine boundary layer, because the latter was subject to wet and dry deposition processes, in contrast to the FT (a discussion of the entrainment process is in the previous chapter). So supply of formic and acetic acids in the area came from the MBL as a background, possibly from local production and possibly from the FT by entrainment.

The results show that the rainwater VWAC of these organic acids varied little from site to site. The precipitation amounts at the different sites were also quite similar, except at La Selva. This implies similar total wet deposition of these organic acids at three of the sites. The column of air scavenged by the falling raindrops increased from the coast to the innermost site in about 350m, this is, 50%. Thus, it is likely that the gas phase levels of formic and acetic acids were either similar at the different sites, or lower at the inland sites. Had there been an increase in the gas phase levels with distance from the coast, a clear increase in the rainwater VWAC should have occurred. Therefore, the total loss of these two acids in the ML had to be

similar or greater than their supply. Now, if an air parcel rained at most once between the coast and the innermost site, the only loss process with an effect on the rainwater contents at the sites was dry deposition. Given that the rainwater contents were similar at the sites, then the loss by dry deposition was similar or greater in magnitude than the supply. But wet deposition of the two acids at the sites was several times the estimated amount of dry deposition, so the total loss by (dry and wet) deposition was several times greater than the supply to the local ML. Therefore, the area under study seemingly represented a net sink for these two acids.

Other biogenic and/or terrigenous solutes.

Table IV-9 shows the site specific VWAC of species potentially having important soil and/or biogenic contributions, namely nitrate, ammonium, calcium and potassium. These species showed a positive concentration gradient in relation to distance from the coast, more clearly seen in Figure IV-8, where the slope of the linear regression gives the approximate increase rates.

Table IV-9. Total and nss VWA concentrations (µM) of the major terrigenous and biogenic species contained in the rainwater samples from Costa Rica.

SITE	Ca ²⁺	±	*Ca ²⁺	±	K^{*}	±	$*K^{+}$	±	NO_3^{-}	±	${\sf NH_4}^+$	±
Tortuguero	1.8	0.4	1.1	0.5	2.3	0.5	1.6	0.6	4.6	0.9	5.3	0.9
Las Ahogadas	1.8	0.5	1.5	0.5	2.5	0.5	2.2	0.6	4.7	1.3	6.3	1.0
La Selva	2.1	0.4	1.6	0.5	3.0	0.5	2.5	0.8	8.3	1.4	9.5	1.4
Veracruz	4.3	0.7	3.9	1.1	3.6	0.6	3.2	0.9	7.2	1.4	6.5	1.0

* marks the nss data

Calcium VWACs increased slightly with distance from the coast up to 60 km, then sharply towards Veracruz, 80 km from the coast. In Veracruz the Ca²⁺ VWAC was significantly higher than at all other sites. Potassium and nitrate VWACs increased more or less linearly with distance from the coast, and they were clearly higher at the two sites with more cultivated land in the vicinity, La Selva and Veracruz. The ammonium VWAC showed a slight increase with distance from the coast, but this increase is comparable to the uncertainty of the values. VWACs for ammonium and nitrate were higher at La Selva than at Las Ahogadas, also 60 km from the coast, and kept out of the general trend.



Figure IV-8. VWAC of major species with possible terrigenous and/or biogenic origin, contained in the rainwater samples from Costa Rica. Higher values at 60 km from the coast correspond to the site La Selva. Lines and slopes were calculated by the least squares method.

In Veracruz there was Ca^{2+} enrichment with respect to all other cationic species (Table IV-10). The Ca^{2+} enrichment factor with respect to the seasalt species was around 3.7, and it was around 1.8 with respect to potassium and ammonium.

 Mg^{+2} K^{+} NH_4^+ SITE / CATION Na⁺ 1 1 1 1 Veracruz Las Ahogadas 1.9 2.1 1.6 2.4 La Selva 2.4 2.3 1.7 3.0 Tortuguero 3.9 3.6 1.6 2.0

Table IV-10. Calcium molar enrichment* factor at Veracruz with respect to cationic species at other sites.

* obtained by dividing the (Ca²⁺ / cation) molar ratio from Veracruz by the one at the site.

The higher potassium and nitrate VWAC at La Selva coincide with a higher formate value, shown in Table IV-8, and could signal to a strong local influence at the site. La Selva had frequent upwind influence from several banana plantations, which the other sites did not, because they were further North. Potassium could have additional sources in the soils and fertilizers from nearby plantations, and this may have resulted in the higher VWAC seen at La Selva. Sites with agricultural influence , as La Selva and Veracruz, are likely to show higher nitrate levels; it is known that fertilization can increase soil emissions of NO_x (Bakwin *et al.*, 1990). Other possible sources of nitrate in the area were oxidation of NO_x formed in lightning or emitted by soils, and nitric acid and PAN formed in smoke or contamination plumes transported above the MBL.

The sharp rise in the calcium VWAC at Veracruz coincides with a decrease in the hydronium VWAC at the site. There is significant anticorrelation between calcium and hydronium content data from Veracruz (R = -0.28; N = 75; slope = -0.46), as discussed in the section devoted to correlations, later in the next section. This points to a neutralizing effect of the calcium containing material on the rainwater. For calcium to imply a neutralizing effect, it had to come from a basic salt, most likely CaCO₃; it is common for CaCO₃ to have a neutralizing effect on rainwater acidity (*e.g.* Sanusi *et al.*, 1996; Almomani *et al.*, 1998). Correction of the hydronium content for a neutralization effect of all non seasalt calcium (3.9 μ M) yields *ca.* 11 μ M H⁺ as the potential VWAC at the site. That is a higher H⁺ VWAC than at the other sites

and coincides with the general increase tendency of the H⁺ VWAC with distance from the coast. The sum of molar equivalents of anions related to acidic species in Veracruz was *ca*. 13 μ M, which roughly coincides with the estimate for H⁺.

The input of basic calcium at Veracruz was equivalent to 45 g ha⁻¹ day⁻¹ CaCO₃ or less. There was a sharp increase in basic calcium input after 60 km, more clearly seen in its enrichment factors relative to other cations (Table IV-10). It is not clear how the sharp increase in basic calcium input after 60 km came about. Several possible mechanisms are mentioned in the following lines.

The acidic red soils in the area were not a likely source of basic calcium, unless they were fertilized with Ca $(OH)_2$ or CaCO₃ when strong convection was taking place, during the daytime, so that some of the calcic dust was incorporated as aerosol into the BL. This was more likely to happen at Veracruz than at the other upwind sites, because there was more cultivated land in the vicinity. However, it would have been a rather occasional source, and the enrichment of calcium in the Veracruz samples was rather constant. Gravel roads upwind from the site could have been a more constant source, at least when dried by the sun; but limestone is not a common component of gravel in the area. Biogenic aerosol could possibly explain the gradual Ca²⁺ increase with distance from the coast up to 60 km, but not the abrupt increase at Veracruz, and also not its apparent basicity.

Long range transport is another possible source for the basic calcium. Calcium carbonate rich aerosol originating in the Western Sahara (Chiapello *et al.*, 1997) could have been transported at relatively low heights above the marine boundary layer without being subject to intense scavenging / washout activity (Prospero and Carlson, 1972; Swap *et al.*, 1992; Moulin *et al.*, 1997a and b; Husar *et al.*, 1997; Formenti *et al.*, 2001). These dust events are relatively common in Summer, and can last weeks. As stated previously, an increase of Z_i at a rate of *ca.* 35 m in 10 km probably occurred. Deepening of the mixing layer with distance from the coast may have downmixed the transported dust into the ML, resulting in eventual scavenging by rain. As stated previously, after 60 km inland, pastures and cultivated land began to predominate in the landscape. A faster increase rate of Z_i –with distance from the coast– over pasture and cultivated land is to be expected (Stull, 1988). Such an increase could have resulted in a sharp rainwater concentration increase of any components that were being transported in the entrained air. Satellite images of aerosols over the oceans and continents could potentially bear proof of aerosol transport towards Central America. Such data are available from several sources (*e.g.* http://jwocky.gsfc.nasa.gov/aerosols/aerosols.html; http://kelvin.nrlmry. navy.mil:9999/aerosol/; etc.), but those found so far unfortunately do not cover the period of interest. So, for the time being, the question as to the actual source of the Ca^{2+} in Veracruz remains open.

IV.4.2.3. Correlations among components at the sites

High correlations among concentration data of different species in a group of samples often suggest common sources of these species or common reactions involving them. In the case of rainwater samples, there are usually high correlations between species simply as a consequence of large dilution factors from one sample to the next. For this reason, it is worthwhile to eliminate outlier data and then consider only the best correlations to be worth any attention.

The concentration data of a selection of ions corresponding to samples from the sites Tortuguero, La Selva and Veracruz were filtered for outliers (median absolute deviation method, Miller and Miller, 1993) and used to obtain correlation coefficients and slopes of the least squares linear fit among them. These values are presented in the following three tables (Table IV-11 through Table IV-13). The higher correlation values are in boldface; the following paragraphs address and discuss some of these.

The major marine aerosol components sodium, chloride and magnesium were the most highly correlated species at all sites. For this reason, sodium alone was used here to represent the seasalt components in the tables, and the data corresponding to Mg and Cl are not shown. Around half of the content of calcium and sulfate at the coast came from seasalt, as shown in Table IV-6; calcium at the coast was best correlated with seasalt. Seasalt correlated similarly well with sulfate at all sites. In contrast, with calcium it did not correlate well at the innermost site Veracruz, which suggests the emergence of other sources of calcium inland.

Sulfate correlated very well with calcium at all sites, except at Veracruz, where its correlation with calcium was not even significant. This shows that the calcium enrichment at that site was not related to sulfate, and thus that the Ca^{2+} was not coming from $CaSO_4$; this is discussed further on in this section. As mentioned in the previous section, about half the sulfate at all

sites was from seasalt. Important local sources of SO₂ in the area would have led to sulfuric acid production and to increase the correlation of sulfate with hydronium. The absence of a comparatively strong correlation of sulfate with hydronium at any of the sites suggests that it was mostly present as particulate neutral sulfate; the generally good correlation of sulfate with aerosol components – as Na⁺, K⁺, Ca²⁺, NH₄⁺ – further supports this. Marine aerosol contains sulfate from two main sources, namely seasalt and gas to particle conversion after oxidation of DMS to SO₂ and finally to sulfuric acid (Warneck, 1988; Seinfeld and Pandis, 1998). Sulfate in the MBL exhibits a bimodal size distribution, with one of the maxima associated to seasalt particles – in the coarse fraction –, and another associated to the accumulation mode and therefore to gas to particle conversion and posterior coagulation (Warneck, 1988).

Nitrate correlated best with hydronium at all sites. This suggests that a large proportion of the nitrate in the rainwater was incorporated as nitric acid, or in any case along with the associated hydronium. Nitric acid can be effectively scavenged by raindrops and cloud droplets; it also condenses on seasalt particles, causing degassification of CO_2 or HCl (Warneck, 1988). HCl is a strong acid that is very effectively scavenged by cloud droplets and rain from the atmosphere. Thus, much of the hydronium originally associated to nitrate was probably scavenged by rain as HCl along with the related nitrate remaining on particulate matter or in droplets (Sanhueza *et al.*, 2001). Nitrate was also highly correlated with sulfate; this suggests the presence of distant anthropogenic sources of SO₂ and NO_x as precursors of these two species; it was not particularly highly correlated with any other species; this suggests that it had multiple source processes.

Calcium was best correlated with sodium at the coast; inland, its correlation with the rest of the cationic species –except H^+ – increased, while that with Na⁺ decreased. At Veracruz there was a negative correlation with hydronium; the only significant anticorrelation in the data set. Most calcium at the coast possibly came in the marine aerosol; this would explain the better correlation with Na⁺ at the coast. The better correlation with NH₄⁺ and K⁺ at the inland sites suggests that its major source there had changed to non seasalt aerosol. The anticorrelation with H⁺ at Veracruz shows that a large fraction of the Ca²⁺ was accompanied by a neutralizing species – most probably carbonate – which raised the pH.

Table IV-11. Correlation coefficients and slopes among some of the analyzed species. Site: TORTUGUERO.

	R	slope	R	slope	R	slope	R	slope	R	slope	R	slope	R	slope	R	slope	R	slope	
ION	Na⁺	Na⁺	${\sf NH_4}^+$	${\sf NH_4}^+$	$K^{\scriptscriptstyle{+}}$	K⁺	Ca ⁺²	Ca ⁺²	for	for	acet	acet	SO4 ^{2⁻}	SO4 ^{2⁻}	NO ₃	NO ₃	H^{*}	H⁺	ION
Na⁺			0.37	2.45	0.44	9.20	0.81	16.68	0.30	5.25	0.27	9.81	0.51	6.58	0.41	3.80	0.52	3.52	Na⁺
${\sf NH_4}^+$	0.37	0.06			0.19	0.59	0.49	1.44	0.59	1.43	0.68	3.44	0.54	0.92	0.47	0.59	0.21	0.22	${\sf NH_4}^+$
K⁺	0.44	0.02	0.19	0.06			0.67	0.64	0.15	0.10	0.32	0.54	0.34	0.21	0.35	0.14	0.27	0.09	K⁺
Ca ⁺²	0.81	0.04	0.49	0.17	0.67	0.69			0.51	0.37	0.50	0.87	0.61	0.39	0.62	0.26	0.54	0.18	Ca ⁺²
for	0.30	0.02	0.59	0.24	0.15	0.24	0.51	0.70			0.84	1.81	0.58	0.45	0.56	0.33	0.40	0.19	for
acet	0.27	0.01	0.68	0.13	0.32	0.19	0.50	0.29	0.84	0.39			0.67	0.23	0.53	0.13	0.45	0.09	acet
SO42 ⁻	0.51	0.04	0.54	0.32	0.34	0.56	0.61	0.96	0.58	0.75	0.67	1.94			0.59	0.39	0.50	0.24	SO4 ^{2⁻}
NO ₃	0.41	0.05	0.47	0.38	0.35	0.88	0.62	1.43	0.56	0.93	0.53	2.16	0.59	0.91			0.66	0.50	NO ₃
H⁺	0.52	0.08	0.21	0.20	0.27	0.81	0.54	1.61	0.40	0.83	0.45	2.30	0.50	1.05	0.66	0.86			H⁺
for = f	ormate	e ace	et = ac	etate	Со	rrelation	significa	ant if R > (0.27 (at	95% con	fidence l	evel)	slop	e: Y is on	sides. X	K above		site Tor	tuguero

	R	slope	R	slope	R	slope	R	slope	R	slope	R	slope	R	slope	R	slope	R	slope	
ION	Na⁺	Na⁺	${\sf NH_4}^+$	${\rm NH_4}^+$	K⁺	K⁺	Ca ⁺²	Ca ⁺²	for	for	acet	acet	SO4 ^{2⁻}	SO4 ^{2⁻}	NO_3^{-}	NO ₃	H^{*}	H⁺	ION
Na⁺			0.48	1.39	0.18	1.48	0.57	5.11	0.43	2.90	0.30	3.98	0.70	4.89	0.21	0.62	0.19	0.62	Na⁺
NH_4^+	0.48	0.16			0.57	1.36	0.75	2.06	0.66	1.42	0.61	2.85	0.62	1.44	0.46	0.50	0.32	0.37	${\sf NH_4}^+$
K⁺	0.18	0.02	0.57	0.24			0.76	0.80	0.22	0.17	0.49	0.93	0.40	0.35	0.43	0.17	0.38	0.14	K⁺
Ca ⁺²	0.57	0.06	0.75	0.28	0.76	0.71			0.41	0.29	0.42	0.75	0.65	0.52	0.47	0.18	0.27	0.10	Ca ⁺²
for	0.43	0.06	0.66	0.31	0.22	0.28	0.41	0.60			0.69	1.54	0.66	0.85	0.45	0.20	0.53	0.26	for
acet	0.30	0.02	0.61	0.13	0.49	0.25	0.42	0.24	0.69	0.31			0.44	0.23	0.39	0.08	0.45	0.10	acet
SO4 ^{2⁻}	0.70	0.10	0.62	0.27	0.40	0.47	0.65	0.81	0.66	0.52	0.44	0.84			0.40	0.19	0.48	0.22	SO4 ^{2⁻}
NO ₃	0.21	0.07	0.46	0.43	0.43	1.12	0.47	1.20	0.45	1.01	0.39	1.80	0.40	0.81			0.52	0.56	NO ₃
H⁺	0.19	0.06	0.32	0.27	0.38	1.01	0.27	0.71	0.53	1.09	0.45	2.06	0.48	1.05	0.52	0.48			H⁺
for = forr	nate	acet =	acetat	e	Correla	tion sigr	nificant i	f R > 0.31	(at 95%	% confide	nce level)	slope: Y	' is on sid	es. X ab	ove		site La	Selva

Table IV-12 Correlation coefficients and slopes among some of the analyzed species. Site: LA SELVA.

	R	slope	R	slope	R	slope	R	slope	R	slope	R	slope	R	slope	R	slope	R	slope	
ION	Na⁺	Na⁺	${\rm NH_4}^+$	${\sf NH_4}^+$	$K^{\scriptscriptstyle{+}}$	K⁺	Ca ⁺²	Ca ⁺²	for	for	acet	acet	SO4 ^{2⁻}	SO4 ^{2⁻}	NO ₃	NO ₃	H⁺	H⁺	ION
Na⁺			0.60	1.92	0.57	3.87	0.41	1.99	0.28	1.25	0.26	2.51	0.58	3.36	0.23	0.44	0.05	0.13	Na⁺
${\sf NH_4}^+$	0.60	0.19			0.58	1.46	0.46	0.83	0.59	1.01	0.47	1.81	0.64	1.25	0.35	0.26	0.27	0.31	${\sf NH_4}^+$
K^{+}	0.57	0.08	0.58	0.23			0.57	0.43	0.22	0.14	0.17	0.25	0.38	0.29	0.12	0.03	0.00	0.00	K⁺
Ca ⁺²	0.41	0.08	0.46	0.25	0.57	0.76			0.04	0.03	0.07	0.14	0.27	0.29	0.13	0.06	-0.28	3 -0.17	Ca ⁺²
for	0.28	0.06	0.59	0.34	0.22	0.33	0.04	0.04			0.83	2.00	0.48	0.56	0.30	0.13	0.63	0.38	for
acet	0.26	0.03	0.47	0.12	0.17	0.11	0.07	0.03	0.83	0.35			0.46	0.25	0.23	0.05	0.48	0.14	acet
${\rm SO_4}^{2^-}$	0.58	0.10	0.64	0.33	0.38	0.49	0.27	0.24	0.48	0.41	0.46	0.84			0.37	0.15	0.22	0.12	SO4 ^{2⁻}
NO ₃	0.23	0.12	0.35	0.45	0.12	0.43	0.13	0.31	0.30	0.68	0.23	1.14	0.37	0.96			0.40	0.50	NO ₃
H⁺	0.05	0.02	0.27	0.23	0.00	0.00	-0.28	-0.46	0.63	1.04	0.48	1.68	0.22	0.43	0.40	0.32			H⁺
for = fo	ormate	acet =	= aceta	ate	Correla	ition sigr	nificant i	f R > 0.28	(at 95%	6 confide	nce level)	slope: Y	is on sid	es. X ab	ove		site Vera	acruz

Table IV-13. Correlation coefficients and slopes among some of the analyzed species. Site: VERACRUZ.

As discussed in the previous section, the potential H^+ content inferred from excess Ca^{2+} in Veracruz samples corresponds well with the increase tendency with distance from the coast seen at the other sites, and with the sum of molar equivalents of the anions. The largest H^+ contributor in Veracruz was nitric acid; whether it reacted with the calcium salt before or after incorporation of the latter into the cloud droplets is not clear.

Potassium generally correlated well with other cations, except H^+ . Its correlation with Ca^{2+} was generally one of the better at all sites. At the coast, it also correlated well with Na^+ , though not with NH_4^+ , while inland it correlated well with NH_4^+ too. The predominant K^+ source at the coast may have been seasalt aerosol, while other sources at the inland sites were likely. Potassium is typically found in biogenic coarse fraction aerosol in large concentrations (Artaxo *et al.*, 1990).

Hydronium showed best correlation with nitrate and sulfate at the coastal site Tortuguero, and with formic and acetic acids in Veracruz, the innermost site. At the intermediate site La Selva it showed similar correlation with all four anions. The increase of nitrate content with distance from the coast does not coincide with an expectable increase of its correlation with H^+ . The anticorrelation with Ca^{2+} contents in Veracruz has already been discussed.

The organic anions formate and acetate show best correlation at all sites among themselves. Next best is their correlation with hydronium, especially that of formate. The latter is not altogether unexpected, because formic acid has a ten times larger dissociation constant than acetic acid.

IV.4.3. The formate / acetate ratio.

Formate and acetate contents in rainwater and in the boundary layer gas phase are most often highly correlated; the two acids share to a great extent production processes as well as loss processes. For this reason it is of interest to calculate the ratio in which the two ions were present in the samples. In this work the HCOOH / CH_3COOH ratio varied between 0.6 and 3.5, with a mean of 1.75 - excluding outliers. The variation of the ratio with distance from the coast did not follow a clear trend (Table IV-14). A strong correlation of the two anions was, however, seen at all sites, as mentioned in the previous section.

The HCOOH / CH₃COOH ratio can be affected by several factors in cloud and rain water. Higher hydronium concentrations favor the release of CH₃COOH more than that of HCOOH from the cloud droplets, due to the 10 times larger acid dissociation constant of HCOOH, as discussed by Andreae *et al.*(1988b). The effect becomes important at pH values approaching 4, and favors higher formate / acetate ratios. Such pH values were rarely observed in the rainwater samples, but are frequent in cloudwater; the air parcels arriving in Costa Rica probably had been subject to a good deal of cloud processing. Additionally, as proposed by Chameides and Davis in 1983 and later modeled by Jacob and Wofsy in 1988, the oxidation of HCHO to HCOOH in cloud droplets could increase HCOOH concentrations – and hydronium, in consequence –, thus directly and indirectly contributing to higher HCOOH / CH₃COOH ratios.

according to sampling site.				
SITE	To coast / km	Ratio VWA	R	H ⁺ / μM *
Tortuguero	1	1.6	0.84	4.6 ± 1.5
Las Ahogadas	60	2.0	0.78	9.6 ± 2.3
La Selva	60	1.7	0.69	6.9 ± 1.7
Veracruz	80	1.4	0.83	3.1 ± 1.0
* \mathbf{H}^{\star} is non-CO ₂				

Table IV-14. Overall VWA Ratios and correlation coefficient of formate with acetate in rainwater, according to sampling site.

At higher pH values, on the other hand, more HCOOH dissociates to formate ion, and fast oxidation of formate ion by HO radicals in the aqueous phase (modeled by Jacob in 1986) would contribute to lower HCOOH / CH₃COOH ratios. So at lower pH values, higher HCOOH / CH₃COOH ratios are favored, while higher pH values contribute to lower the ratio. The latter should then be observable if, by some external contribution, part of the hydronium ions in the cloud droplets were neutralized, thus raising their pH. This is what happened at the site Veracruz, where higher pH values were apparently caused by a basic calcic salt.

Site specific hydronium VWA concentrations plotted against the corresponding VWA ratios had a good linear relation, as shown in Figure IV-9; the uncertainty of the data is near 25% (Table IV-8).



Figure IV-9. VWA of the formate / acetate ratio plotted against the hydronium concentration beyond pH = 5.6, evaluated from the sets of all selected data from the individual sites. R is the correlation coefficient; the correlation is significant at 98% confidence (P = 1.5%).

In spite of the high uncertainty of the plotted data (*ca.* 25%), lower ratios do coincide with lower hydronium concentrations and *viceversa*, and the VWA ratio at Veracruz, the site where apparent neutralization of hydronium by a basic calcium salt occurred, is the lowest of all. This agrees qualitatively with the prediction of Jacob (1986) –mentioned in previous paragraphs–, that higher pH values would contribute to faster depletion of formic acid by oxidation of formate ions with HO radicals.

As pointed out in the previous chapter, it was observed in the gas phase in Sipaliwini that the $HCOOH / CH_3COOH$ ratio showed a similar variation to that of the O₃ levels. The rainwater data from Costa Rica were examined for this relationship and it was also found to occur. As shown in Figure IV-10, there is a good linear relation, significant at the 98% confidence level. A possible explanation to this is that several acidic species (*e.g.* nitric acid, sulfuric acid, organic acids and CO₂) are produced in greater amounts in air parcels transporting large amounts of ozone precursors. During cloud processing, higher acidity in the cloud droplets inhibits destruction of formate, favoring higher HCOOH / CH_3COOH ratios. So higher O₃

levels would probably tend to coincide with higher acidity and higher gas phase and aqueous phase $HCOOH / CH_3COOH$ ratios.



Figure IV-10. Linear relation of the formate / acetate ratio in rainwater in Costa Rica to the ozone levels. The ozone data are afternoon means. The ratios are volume weighted means.

IV.4.4. Concentration variation during individual events.

One popular notion regarding the variation of concentrations in rainwater during an event is that they always decrease in time, as water soluble gases and particulate matter are progressively scavenged. This view does not distinguish in-cloud scavenging from under-cloud scavenging. A more elaborate interpretation is that the lowest concentrations during an event correspond to the in-cloud concentrations of solutes, while the higher concentrations are due to under-cloud scavenging and evaporation of the droplets during their fall. Consideration of some processes occurring in a raining cloud helps to complete the latter interpretation.

At the cloud's edges there is entrainment of drier air from the surroundings, which leads to evaporation of the droplets and to scavenging of larger volumes of air, and therefore to higher concentrations of the scavenged species in the cloud droplets near the edges of the cloud. So the raindrops falling from the edges of the cloud tend to be more concentrated, fewer and smaller, and the column of air through which they fall is drier, thus favoring evaporation. On the other hand, larger and more diluted drops precipitate from the central region of the cloud, and they fall through an air column that is more humid and washed out by rainfall than under the edges of the cloud. As a result, concentrations of rainwater are higher under the edges of the raining cloud. So the concentration of the solutes is usually higher at the beginning of an event, then decreases while the precipitation rate increases, and often increases towards the end of the event, while the precipitation rate dwindles (Pruppacher and Klett, 1997).

Few studies exist addressing the variation of solutes concentration in rainwater as an event elapses (*e.g.* Lacaux *et al.*, 1992a; Kawamura *et al.*, 1996a; Pruppacher and Klett, 1997 and references therein). In the case of organic acids, the issue is usually addressed only marginally. Lacaux *et al.* (1992a) averaged four similar events of rain from convective clouds sampled in Congo, in a forested area, and grouped the solutes in H^+ , organic acids (formic and acetic), inorganic anions (nitrate, sulfate and chloride), and cations (calcium, sodium, ammonium and potassium). They found that, in general, the concentrations of solutes decreased as the event elapsed, but the inorganic anions and the cations did so at a faster rate than H^+ and the organic acids. They explain the slow decrease of H^+ content as due to the slower decrease of the organic acids content, and to a neutralizing effect of the particulate matter, uptaken mostly at the beginning of the event (evidenced by higher cations contents).

Kawamura *et al.* (1996a) refer also marginally to the variation, during events, of concentration ratios of organic acids to aldehydes, of the diacid / monoacid ratio and of the HCOOH / CH_3COOH ratio. They discuss in terms of preferential uptake of one or another solute, the Henry partition coefficients of the solutes, and possible oxidation of aldehydes to acids, to interpret their results. They found that the HCOOH / CH_3COOH ratio tended to decrease from the first to the second sample collection, and interpret d that as a result of preferential scavenging of HCOOH.

In this work, it was found that the deposition rates of the solutes (amount of deposed substance in time) decreased in time quite consistently to a minimum value that was maintained until the end of the events. The first and / or second samples were in the rule the most concentrated of each event. Similar to that observed by Lacaux *et al.*(1992a), usually at least 50% of the deposed solutes were in the first 30% to 40% rainwater volume.

Concentration variations of formate ion within an event were found to be representative of those of other solutes. Figure IV-11 shows the variation of the concentration of formate in the three most voluminous events at La Selva. The concentrations of other solutes showed essentially the same variation pattern. The first and shortest of the three events showed initial concentration decrease followed by consistent increase during the second half of the event. The second and third events showed concentration decrease in time and light increase toward the end, when the rainfall had diminished to a light drizzle. The event occurring on July 24 (third plot) had several hours drizzle, during which an essentially constant concentration was observed.

The rate of deposition showed clear decrease in time during the events, except for a data point in the event of July 22. Practically all the deposed solutes fell within the first 40 to 60 minutes; subsequent rainfall had little net effect regarding deposition, even though concentration increased towards the end of the events. In the event of July 24, the maxima of deposition and precipitation rates did not coincide, while in the other two it did; the latter was more often the case in this work.

The trends observed in this work for variation of concentrations throughout an event adjust well to that reported and discussed by Pruppacher and Klett (1997), regarding the higher concentrations under the edges of the raining cloud.

The data sets were also examined for some of the regularities reported by Kawamura *et al.* (1996a) and Lacaux *et al.* (1992a). The HCOOH / CH_3COOH ratio did not show the decrease in time reported by Kawamura *et al.* (1996a), but in about half the cases did show lower values in the middle of an event, similar to that observed for concentrations. This, however, was not an absolute rule; the ratio often showed either a constant increase or a constant decrease tendency throughout an event. Possibly, the air column under the clouds in Costa Rica was cleaner, making under cloud scavenging less significant for the final rainwater composition.



Figure IV-11. Formate content and precipitation rate during three selected events at La Selva. Error bars represent the uncertainty of the concentration measurement.

The deposition of the species coming from particulate matter (cations, sulfate, nitrate, seasalt components) was not found to be as a rule faster at the beginning of the events than the deposition of formate, acetate or H⁺, as has been reported by Lacaux *et al.* (1992a) regarding samples collected in Congo. In most events examined in this work, the relative rate of deposition (% of the total per time unit) was similar throughout the event for all species and groups (organic acids, inorganic anions, seasalt, cations and H⁺). Exceptions with higher relative rates for organic acids or H⁺ were not less frequent than exceptions with higher relative deposition rates for cations, seasalt or inorganic anions. Possibly, a much greater proportion of the solutes in the samples collected by Lacaux *et al.* (1992a) was scavenged under the cloud, and this caused the differences in the deposition rates observed by them. In fact, as reported by Lacaux *et al.* (1992a), the air under the raining clouds in Congo was significantly laden with aerosols, gases, smoke, etc. The air under the raining clouds in Costa Rica was probably much cleaner, being it from the marine boundary layer and not affected by biomass burning or other nearby contamination sources.

Important variations within an event in the HCOOH / CH_3COOH ratio related to the calcium and H^+ content were not observed, as might have been expected (see previous section).

Possibly, a finer time resolution of the sampling could lead to better insight into the tendencies taking place throughout events; a good choice could be increasing the time resolution at the beginning of the events. Sampling cloud water with balloons, kites or model airplanes is also an interesting possibility to study the chemistry taking place in different regions of clouds.

IV.5. Chapter conclusions

The observed O_3 levels were comparable to values recorded at Barbados (Sanhueza *et al.*, 2000), if loss by dry deposition in Costa Rica is considered. Some variations in the O_3 levels during the sampling period were apparently related to the history of the air parcels, that is, to long range transport of O_3 .

Consideration of the dynamics of the marine boundary layer when advected over land has been a key for the analysis of the results obtained in Costa Rica, just as well as for the results from Surinam (previous chapter).

The analyzed species showed groups according to the variation of their VWAC in rainwater with distance from the coast. Marine aerosol related species (seasalt, sulfate, magnesium), and land surface related species (ammonium, nitrate, potassium, calcium) showed opposite variation with distance from the coast: the latter increased while the former decreased, as had been expected. The seasalt aerosol depletion rate was comparable to that calculated for air masses advected into the central Amazon from the Atlantic (Andreae *et al.*, 1990). Calcium, in contrast to the nitrate, potassium and ammonium, showed a particularly sharp concentration increase from 60 to 80 km inland; long range transport of dust containing calcium carbonate, likely from the Western Sahara, was the most likely cause.

The rainwater contents of organic acids did not show a clear trend with distance from the coast; the contents were rather similar at the different sampling sites. This suggests that the gas phase levels of HCOOH and CH₃COOH at these sites did not increase with distance from the coast and probably did not differ greatly. From here, dry deposition, estimated in *ca*. 10 μ mol m⁻² day⁻¹ in the area, must have been similar to the sum of local production and incorporation from the FT. Wet deposition amounted to several times the estimate for dry deposition. So, adding wet deposition, the area under study apparently was a net sink for HCOOH and CH₃COOH during the sampling period.

The pH of the rainwater samples was apparently a determining factor for the formate / acetate ratio in two ways. In rainwater with higher pH values, the ratio was lower than in more acidic rainwater. The calcium enrichment observed in Veracruz coincides not only with higher pH
values, but also with lower formate / acetate ratios. Seemingly, neutralization by the basic calcium salt allowed depletion of formate by oxidation with HO radicals in cloud droplets and in the water film of particles; this probably occurred during cloud processing.

Covariation of the formate / acetate ratio with gas phase O_3 levels was observe just as well. The latter confirms the observation made in the gas phase measurements made in Sipaliwini during the LBA-CLAIRE campaign (previous chapter), and extends the covariation to the aqueous phase. A likely reason for this covariation is that ozone and acids precursors usually coincide in air parcels affected by smoke and other anthropogenic contaminants. This carries the implication that both the O_3 and the acids contents of air parcels brought by the Trades to the tropical American Atlantic coast are a consequence of remote emissions, mostly coming from Africa and Europe.

The main sources of H^+ in the area were apparently formic, acetic and nitric acids, as indicated by the strong correlations of the three anions with hydronium. While this role was expected of the organic acids, it was not expected of nitric acid, mainly because its source processes in the area were initially supposed to be insignificant. As it turned out, nitric acid had large enough local source processes for its concentration in rainwater to clearly increase with distance from the coast, something not observed in HCOOH and CH₃COOH. Nitric, formic and acetic acids had several likely source processes in the area, including long range transport of smoke and contamination plumes.

Compositional variation of the rainwater during individual events showed that most of the wet deposition of solutes occurred within the first 20 to 40 minutes. It was frequent for concentrations to be lower in the middle of the events, and the deposition rate was the only parameter to decrease consistently toward a minimum in all events. The formate / acetate ratio did not show a consistent variation pattern during events, as has been observed by Kawamura *et al.* (1996a) in Californian urban samples; this was possibly a consequence of having a cleaner air column under the cloud in the Costa Rican Northeastern plains. In contrast with previous observations (Lacaux *et al.*, 1992a; Kawamura *et al.*, 1996a), no clear differences in deposition rates were observed from one species to the next; this was another apparent consequece of the lower levels of the species in the air column under the cloud in the Costa Rican Northeastern plains.

Glossary and List of Abbreviations

Ac	acetate
AEC	Anion Exclusion Chromatography
asl	Above Sea Level
AVHRR	Advanced Very High Resolution Radiometer
BL	Boundary layer
BOVOC	biogenic VOC
cf.	<i>confer</i> , compare
CMDL	Climate Monitoring and Diagnostics Laboratory, NOAA.
CML	Convective mixed layer
CML Mean	afternoon average; here from 11:00 or 12:00 to 16:00 or 17:00 LST.
CPTEC	Centro de Previsão de Tempo e Estudos Climáticos, INPE, Brazil.
CZE	Capillary Zone Electrophoresis
e.g.	exempli gratia
EARTH	Escuela de Agricultura de la Región Tropical Húmeda
ENSO	El Niño southern oscillation
EZ	Entrainment Zone
FLPE	fluorinated polyethylene (high density)
For	formate
FT	Free troposphere
GPS	global positioning system
HAc	acetic acid
HDPE	High Density PolyEthylene
HFor	formic acid
НМНР	hydroxymethyl hydroperoxide
HPyr	pyruvic acid
HRS	highly reactiv sesquiterpenes
i.e.	<i>id est</i> , that is
ibid	<i>ibidem</i> , at the same place
IC	Ion Chromatography
idem/eidem	the same author/ the same authors
IMAU	Institute for Marine and Atmosphere Research of the University of Utrecht.
INPE	Instituto Nacional de Pesquisas Espaciais, Brazil.
isocratic	chromatography using a mobile phase of constant composition
ITCZ	intertropical convergence zone
IVIC	Instituto Venezolano de Investigaciones Científicas (Laboratorio de Química Atmosférica).
KNMI	Royal Dutch Meteorolgy Institute
LAC-group	group of anions eluting with similar T_R as lactic acid.

LAQAT	Laboratorio de Química de la Atmósfera (UNA, Costa Rica).
LBA	large scale biosphere-atmosphere experiment in Amazonia
loc. cit.	loco citato, in the place cited
LOD	limit of detection
LST	local standard time
Μ	Molar concentration in solution, mol / Liter
MHP	methyl hydroperoxide
ML	Mixing Layer
MPI	Max Planck Institute
MPIC	Max Planck Institute for Chemistry.
MSA	MethylSulfonic Acid
NBL	Nocturnal Boundary Layer
NMHC	Non Methane HydroCarbon
nmol mol ⁻¹	nanomol per mol, equivalent to 1 molecule in 10 ⁹
nss	non sea salt
ОМР	Observatoire Midi-Pyrénées, Toulouse, France
op. cit.	opere citato
OTS	Organization for Tropical Studies
PACR	PeroxyACyl Radical
PAN (s)	PeroxyAcyl Nitrate (s)
PBL	Planetary Boundary Layer
PTFE	PolyTetraFluoroEthylene
PVC	PolyVinyl Chloride
Pyr	pyruvate
R _D	Deposition rate
RL	Residual Layer (nocturnal)
sd	standard deviation
ТВАОН	TetraButylAmmonium hydroxide
Тм	Migration time (analogous to T_R ; used in CZE).
T _R	Retention time (used in chromatography).
ТТАН	TetradecylTrimethylAmmonium Hydroxide
UNA	Universidad Nacional, Heredia, Costa Rica
V _d	deposition velocity
VMR	Volume Mixing Ratio
VOC	Volatile Organic Compounds
VWM or VWA	Volume Weighted Mean or Average
VWAC	Volume Weighted Average Concentration

Additional Data Graphs from LBA-CLAIRE



Figure A1-1: Overall hourly averages of wind speed in Sipaliwini. All data included.



Figure A1-2: Overall hourly averages of ozone in Sipaliwini. All data included.



Figure A1-3. Wind speed, CO and ozone on individual days in Sipaliwini.



Figure A1-4. Wind speed, CO and ozone on individual days in Sipaliwini and hourly averages for whole sampling period.



Figure A1-5. HCOOH and CH₃COOH volume mixing ratios on individual days in Sipaliwini.



Figure A1-6. The HCOOH / CH₃COOH ratio on individual days in Sipaliwini.

Backtrajectory Plots for LBA-CLAIRE





Figure A3-1. Three 10 day back trajectories ending on March 14 in the Surinamese afternoon mixing layer, and starting near or in the African boundary layer. Contribution of the KNMI to LBA-CLAIRE.





Figure A3-2. Three 10 day back trajectories ending on March 15 in the Surinamese afternoon mixing layer, and starting near or in the African boundary layer. Contribution of the KNMI to LBA-CLAIRE.



Figure A3-3. Three 10 day back trajectories ending on March 23 in the Surinamese afternoon mixing layer, and starting near or in the African boundary layer. Contribution of the KNMI to LBA-CLAIRE.





Figure A3-4. Two 10 day back trajectories ending on March 24 in the Surinamese afternoon mixing layer, and starting near or in the African or South European boundary layer, and one starting in the Canadian BL. Contribution of the KNMI to LBA-CLAIRE.

Backtrajectory Plots for the Field Work in Costa Rica, 1996.

The backtrajectory calculations and plots contained in this appendix were provided by the NOAA's Climate Monitoring and Diagnostics Laboratory (CMDL). The method used was that of Harris and Kahl (1994).

All plots presented in this appendix correspond to 10 day backward calculations. For each day, three arrival heights have been calculated: 500 m, 1000 m and 2000 m. For each day and arrival height, there are two calculations, one with arrival time 00:00 UT (= 6:00 LST) and one with arrival time 12:00 UT (= 18:00 LST).

appendix 4



Figure A4-1: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 12, 1996. Arrival height: 500m.



Figure A4-2: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 12, 1996. Arrival height: 1000m.

appendix 4



Figure A4-3: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 12, 1996. Arrival height: 2000m.

appendix 4



Figure A4-4: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 17, 1996. Arrival height: 500m.



Figure A4-5: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 17, 1996. Arrival height: 1000m.

appendix 4



Figure A4-6: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 17, 1996. Arrival height: 2000m.

appendix 4



Figure A4-7: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 24, 1996. Arrival height: 500m.



Figure A4-8: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 24, 1996. Arrival height: 1000m.

appendix 4



Figure A4-9: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 24, 1996. Arrival height: 2000m.

appendix 4



Figure A4-10: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 127, 1996. Arrival height: 500m.



Figure A4-11: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 27, 1996. Arrival height: 1000m.

appendix 4



Figure A4-12: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 27, 1996. Arrival height: 2000m.



Figure A4-13: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 29, 1996. Arrival height: 500m.



Figure A4-14: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 29, 1996. Arrival height: 1000m.

appendix 4



Figure A4-15: Ten day backtrajectory plot for the Northeastern plains of Costa Rica on July 29, 1996. Arrival height: 2000m.

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LEBENSLAUF

Name:	Jaime F. Quesada Kimzey
Adresse:	Escuela de Química, Universidad Nacional, Heredia, Costa Rica.
Geboren:	Los Angeles, California, USA. 25.7.1963
Staatsangehoerigkeit:	Costa Rica / U.S.A.
Familienstand:	Verheiratet (10.94)
Berufstiteln:	Licenciado en Química Inorgánica e Industrial. (Universidad de Costa Rica, April, 1991).
Ausbildung:	
Grundschule:	Justo Sierra Grundschule (Morelos, México). 1969-75.
Schule:	Mehrere in Mexiko und Costa Rica; Dez. 1982.
Hochschule:	U.C.R. <u>Licenciatura en Química</u> , Maerz 1991. These: <u>Studie, Synthese und Charakterisierung einiger Nikotinaten</u> <u>von Chrom (II) und Vanadium (II).</u> (Jan. 1991).

Anstellungen:

- Beauftragter des Labors fuer Chemie und Boeden der EARTH (Escuela de Agricultura de la Región Tropical Húmeda). 02.91 08.1992
- Wissenschaftlicher Mitarbeiter des Laboratorio de Química de la Atmósfera (*LaQAt*), an der Universidad Nacional, Costa Rica. 10.92-03.1994
- Wissenschaftlicher Mitarbeiter des *LaQAt* und Lehrer an der Universidad Nacional, Costa Rica. 02.2000 bis heute.

Studentenanstellungen:

- -Assistent zum Kurs Analytische Chemie I fuer Chemiestudierende, UCR. (1 Sem.).
- -Assistent zum Kurs Anorganische Chemie I, UCR (3 Sem.).
- -Assistent zu Theorie- und Laborkurse: Anorganische Chemie II, UCR. (2 Sem.).
- -Assistent zum Kurs Fortgeschrittene Techniken der anorganischen Chemie.(2 sem).
- Forschungsassistent bei Prof. Dr. C. A. Murillo 1988-91.

Veroeffentlichungen:

"Solid Solutions of a Jahn-Teller Compound in an Undistorted Host..." Cotton, F.A.; Falvello, L.; Ohlhausen, E.L.; Murillo, C.A.; Quesada, J.F. *Zeitchrift der anorganischen und allgemeinen Chemie*, **1991**, *598/599*,53-70.

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Interessen:

- Entwicklung kostenguenstiger Sensoren und Systemen zur Messung von Umweltvariablen in Entwicklungslaender.
- Forschung der tropischen Troposphaere, insbesondere der von Regenwaelder beeinfluesster Troposphaere.
- Etablierung eines Netzes zur Beobachtung der Luftqualitaet im zentralen Bereich Costa Ricas.
- Neue Entwicklungen in der Lehre der Naturwissentschaften, die besonders guenstig sind fuer Entwicklungslaender.
- Etablierung eines Mechanismus und/oder Unternehmen zur Stiftung, Entwicklung und Marketing von Hi-tech Erfindungen und Ideen in Costa Rica und Mittelamerika.

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