Atmos. Chem. Phys. Discuss., 7, S3546–S3560, 2007
www.atmos-chem-phys-discuss.net/7/S3546/2007/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Tropospheric OH and Cl levels deduced from non-methane hydrocarbon measurements in a marine site" *by* C. Arsene et al.

C. Arsene et al.

Received and published: 31 July 2007

Interactive comment on "Tropospheric OH and Cl levels in a marine site" by Arsene et al. Arsene et.al.

We would like to thank referee #1 for his comments to the manuscript. Our answer is addressed here down and parts of the observations are implemented in the final revised version of the manuscript.

The aim of this article is not "to expand on previous analysis methodologies and provide a new insight on tropospheric Cl chemistry". The present work aims to provide, for the first time to our knowledge, information on the seasonal variation of OH and Cl radicals in a polluted marine site, by using well established methodologies. For this, we first bring evidence for the existence of Cl radicals in the area using already published

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

and well established methodologies and, secondly, using the methodology employed by Rudolph et al. (1997) we estimate the OH/Cl ratio (based on several hydrocarbon pairs). Then instead of using a mean value for OH radicals, as done in several works up to now, we estimate OH radical concentration from the day-time hydrocarbons variability and compare it with the results from a 0-D box model. Previous work (Vrekoussis et al., 2004) has shown that the applied 0-D box model reproduces reasonably well the measured OH radical concentrations in the area. Regarding the OH radical, the good agreement between the concentrations deduced both from the hydrocarbons variability and the 0-D box model increases our confidence in the present used approach. Finally, from the estimated OH concentrations, we are able to deduce Cl levels on a seasonal basis. To our opinion this is useful information for the scientific community as all up to date published studies on the seasonal variability of Cl radicals purely rely on modelling exercises. Indeed, the aim of this article was achieved using “old” science but this do not necessarily mean “bad” science.

Answer to the comments on the Experimental Section

The measurement sites are categorised using Van Dingenen et al. (2004) and Putaud et al. (2004) definition. Distance of a station from large pollution sources such as cities, power plants and major motorways, and the traffic volume are major criteria used in this classification. Accordingly with this, a natural background correspond to a site with a distance from large pollution sources $>$50 km, while a rural background has a distance from large pollution sources between 10-50 km.

P6332, L8: Technical suggestion. It was changed accordingly in the revised version

P6332, L10-12 Crete is a relatively large island (the fourth in size in the Mediterranean) and hence local influences can be both of biogenic and of anthropogenic origin. In order to avoid such influences, air samples should be collected under wind of N direction. This wind direction occurs during the whole year (frequency of 50% of the total cases) and it prevails during summer (more than 70%) (Mihalopoulos et al., 1997). Previous work performed on this island, and especially at Finokalia station (Kouvarakis et al., 2000), showed that when the air masses are sampled under the N sector influence, the obtained results (in terms of chemical composition of the atmosphere) can have a regional rather than a local significance. As our aim is to investigate the seasonal variation of Cl atoms under conditions of regional rather than local significance, our sampling strategy was oriented to periods of N winds with relatively high speed. The importance of data collected under local conditions for the scientific community is questionable. However, since the word "important" used in the manuscript seems to mislead the reader (we don't mean that local influence is important in terms of frequency) we have rephrased this part of the discussion in the revised version of the manuscript.

P6332, L14-16 We understand the reviewer's concern on the missing 8-hours measurements that are definitely needed to construct a complete diurnal cycle. However, the aim of the present work can be achieved without such data as explained below. An important point in the present manuscript is the estimation of the OH radical concentrations based on the hydrocarbons variability observed during the day-time (in order to estimate Cl from the OH/Cl ratio). In the present work the strategy of hydrocarbon measurements was focused on the period from 7:00-22:00, summer local time, as it can represent without any bias hydrocarbons variability during day-time. Any additional period would be not useful in the estimation of the OH levels as during night-time hydrocarbons variability is not governed by the OH radical sink (expected to be very low) but mainly by exchange in the sources strength. The levels of the OH radicals estimated using complete 24h measurements, performed in a preliminary work at the natural site with an automatic gas chromatographic system (able to measure mainly alkanes and isoprene with time step of 1h) (Liakakou, 2007), are in very good agreement with those independently estimated in the present work. This observation has increased our confidence in the obtained results. Unfortunately, the number of compounds measured with the automatic technique (Liakakou, 2007) was not sufficiently high in order to apply with confidence the variability concept proposed by Rudolph et al. (1997) and, hence, a comparison for possible Cl atom concentration at the same site is not possible. A short paragraph with these details has been added in the revised version of the manuscript.

P6332, L18-20 The measurements for the hydrocarbons were performed in collaboration with Dr. Bernard Bonsang (LSCE/CNRS, France) who has more than 30 years experience in the topic and participated in several international inter-comparison studies regarding atmospheric level of hydrocarbons. The analytical set-up developed by Dr. Bernard Bonsang has been applied in this work, a common standard has been used and several inter-comparisons have been performed between the two laboratories using common samples and standards. The questions raised by the referee are answered in Bernard Bonsang's previous work, performed since 1985. We feel that repeating this type of work is firstly not original and secondly out of scope of the present article. However, to answer the referee's requirements below we provide answers to his concerns and part of these answers have been introduced in the manuscript. -The analytical procedure developed in the present work is based on that described initially in Bonsang and Lambert (1985) and largely improved since then accordingly with more recent works (Boissard et al., 1996, Bonsang and Kanakidou, 2001). The method is also suitable to quantify heavier hydrocarbons, at pptv levels, and has been also validated during intercomparison exercises (Apel et al., 1994). -For the on-line procedure the sample transfer line, made of silica-lined stainless steel tube (5 m x 1/8" O.D., Silicosteel, Restek, Bellefonte, USA) was connected to a 6 port valve (Valco) made of the same chemical constituents. Silica-lined stainless steel (tubing, valves) are known to assure a relatively high degree of chemical inertness (Plass-Dulmer et al., 2002). Liakakou et al., (2007), in a study performed by using an automatic gas chromatographic system, report sampling of hydrocarbons at a flow of about 30-50 cm3 min-1 through a similar transfer line. -In the present study, each on-line measurement started with an initial flushing of the entire sampling line with air at 50 mL min-1 in order to ensure surfaces preconditioning (an adsorption - desorption equilibrium with the sample air is established). -In addition a number of tests have been performed with simultaneous canister measurements: i.Hydrocarbons were also collected simultaneously with the on-line measurements in stainless steel canisters and analyzed immediately after the end of the intensive campaigns. The agreement of the analysis by the two methods was within 2% and has increased our confidence on the experimental set-up employed for the on-line measurements. ii.Randomly selected stainless steel canisters containing hydrocarbons collected in Crete, Greece (natural and rural locations) were also analyzed at CNRS/CEA, France (by Bernard Bonsang), within a period of 2 weeks after the sampling has been undertaken (hydrocarbons sampled in stainless steel canister are stable for a period of 6 months after collection, Kanakidou et al., 1988, 1989). Again the agreement was very good (of the order of 2%) and this has confirmed the validity of our system. iii.The primary standard calibration mixture has also been analyzed in the two laboratories (Greece and France) and the agreement was within 1%. -Tenax TA (poly-2,6-diphenyl-p-phenylene oxide, 60/80 mesh), used in the analysis of heavy and light hydrocarbons (Komenda et al., 2001), was packed into a stainless steel tube (180 mm x 1/8") and fixed with silanised glass wool. Prior analysis the trap was conditioned for 3 hours at 523 K by flushing it continuously with He-5 at 30 cm3 min-1. -The specific temperature of ethanol and liquid nitrogen mixture (-100 oC ś 5 oC) was used for a quantitative adsorption of hydrocarbons on the Tenax TA, while at this temperature the main constituents of the sample air, N2, O2, and CO2, passed through the trap without condensation. Moreover, the adsorption efficiency has been previously checked at different temperatures, and it has been observed that the range -90 oC to -120 oC represents the suitable temperature domain for quantitative adsorption of C2 hydrocarbons. -The collected sample was thermally desorbed into the trap containing non-silanized glass beads (60/80 mesh) packed into a stainless-steel tube (100 mmŒ1/16") which was kept at the liquid nitrogen temperature (-196 oC). The cryogenic pre-concentration step on glass beads helped to increase sensitivity in the determination (peak broadening effect was also diminished) and removes CO2. -The thermal desorption in both cases (Tenax TA and glass beads traps) was ensured by heating the 1/8" and 1/16" tubes at 100 oC, temperature which has been found to be adequate for complete desorption of the retained hydrocarbons. -Magnesium per-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

chlorate (Mg(ClO4)2) filled in a 200 mm x 1/4" Silicosteel tube was used to remove the humidity which could produce several problem (clogging of the system, extinguishing of the FID detector, changes in the retention time and elution order of the hydrocarbons from the column). It was frequently replaced (each set of 5 measurements).

P6332, L26: Technical suggestion. It is changed accordingly with the suggestion in the revised version

P6333, L2: Technical suggestion. It is changed accordingly with the suggestion in the revised version

We agree that the Rt-Alumina, Al2O3/KCl, PLOT capillary column is not the ideal for the analysis of larger than C7 hydrocarbons. With the specific type of column the reproducibility was lower than 2% for hydrocarbons up to toluene (C7) but for the hydrocarbon with carbon number greater than C7, indeed, the reproducibility is decreasing (20% or greater, ethyl benzene for example). Note that, in the present study we do not use any hydrocarbon from the C7-C8 range for the estimation of the OH and Cl concentrations as C4-C6 compounds were mainly used. PLOT Alumina capillary column often is used in long-term measurements of hydrocarbons in the C2-C8 range (Kanakidou, 1988; Plass-Dulmer et al., 2002; Steinbacher et al., 2005; Hakola et al., 2006; Read et al., 2007, PLOT Al2O3/KCl; Hopkins et al., 2005; Durana et al., 2006, PLOT Al2O3/Na2SO4). From the analytical point of view, the performances of the procedure employed in the present work have been previously checked and details are presented in Bonsang and Lambert, 1985; Bonsang et al., 1987; Bonsang et al., 1988; Kanakidou et al., 1988; Bonsang and Kanakidou, 2001). However: -Over the course of measurements performed from February 2006 to May 2007 (although the present work reports only on data from March 2006 to October 2006) the detector response to a 50 ul of the 100 ppmv standard gas mixture (Air Liquid primary standard) or to 1 ml of the 1 ppmv standard (Restek, a secondary standard calibrated versus an Air Liquid primary standard) has been checked and found to vary by less than 5% with no systematic change in response all year long. During the same day of analysis, the response of the detector remains constant within less than 1%. -Taking into account the linearity of the FID detector over a wide range, the calibration was performed regularly by injection of 50 ul of the standard mixture containing 100 ppmv of major C2-C4 hydrocarbons. The standard it consisted of ethane (104 ppm), ethene (110 ppm), propane (104 ppm), and n-butane (100 ppm) in N2 and its stated accuracy was 2%. This calibration procedure, previously described in details (Bonsang and Lambert, 1985; Boissard et al., 1996), is equivalent to the injection of 5 ppbv hydrocarbon for a typically 1000 ml air sample. This method has been also validated during intercomparison exercises (Apel et al., 1994). The reproducibility of the standard was better than 1% and the overall reproducibility of the analysis of the order of 2%. The detection limit was of the order of 2 to 5 pptv for the C2-C3 and the C4-C6, respectively and the precision of the analytical technique was previously evaluated by Boissard (1992) to be within 6%. The certified gas standard mixture of 100 ppmv (certified accuracy of ś2%), was used as a primary calibration standard. The “injected daily with a pressure-lock syringe” does not necessarily mean that the primary calibration standard was injected only once per day (during intensive of few days/month, primary calibration standard was injected at the beginning and at the end of each measurement day). The reproducibility of sequential primary calibration standard injection (sets of 10 identical injections) is less than 0.5%. -Apart of the 50 ul, different volumes (10, 100, 150, and 200 ul) of the primary and secondary calibration standard were also analyzed and, in this range, the detector response was linear (response signal was directly proportional to the injected volume of the standard). -All the compounds were quantified on the base of the assumption of a uniform per-carbon response (C-response). Taking into account the linearity of the FID detector with respect to the carbon number of the molecules detected, this calibration based on the FID detector response to C2-C4 hydrocarbons is also suitable to quantify heavier NMHC, at pptv levels, with accuracy better than 2% from a compound to another. Individual response factors of different hydrocarbons were investigated accordingly with the method described by Komenda et al. (2001). -Per-carbon response factor of an FID detector to various carbon number on per molecule basis is used also in other investigation (Yang et al., 2005). -However, in the present work acetylene has been quantified on a similar procedure. Indeed, it has been observed that the carbon response for acetylene is a little lower (of the order of 10%) than for other hydrocarbons, for which the response per carbon is identical, and remains within the range of accuracy of the measurements (lower than 2%). Acetylene, however, is usually used for its relative variation and as a tracer of contaminated air masses transported from polluted areas. -“Accuracy of the measurements of about 10%” is the result of the analysis concerning the closeness of the agreement between the result of the measurement and their possible true value (standard and samples). -Precision is highly dependent on the distribution of possible random errors and is calculated as standard deviation of test results. It includes the reproducibility of the measurements (upper limit of 2%), standards uncertainty (2%), volume readings (1%), and peak area integration error (maximum 1%, but with large relative error when peak size is approaching the detector noise response and with very small relative error in the case of sharper peaks). The sum of these errors did not approach the upper quoted limit for uncertainty (10 pptv). Major source uncertainties in the analysis were identified accordingly with the EURACHEM/CITAC Guide (2000).

Answer to the comments on the Results Section

About data presented in Figure 1 The suggestions proposed by the referee for stylistic and technical corrections are already taken into account in the corrected version of the manuscript. -We agree with the referee that for a complete diurnal variability a full cycle of measurements is needed. However, this is out of the scope of the present work. For accuracy and to satisfy the requirement, in the revised version we have replaced the term diurnal variability with diel variability since the measurements have been performed from 07:00 to 22:00 during the summer intensive (diel is substituting diurnal also upon second referee’s observation). However, earlier work by Liakakou (2007) confirms that 07:00 to 22:00 period can reproduce without bias the diurnal variability of the hydrocarbons. Note that for the OH determination we use the maximum (early morning) and the minimum (around 18:00 - 19:00 summer local time) values. Thus even using this shorter sampling duration the conclusions of our work are not affected. -i- and n-pentanes are about 4 and 15 times more reactive toward OH when compared with propane and ethane, respectively. Thus a stronger variability is expected to be observed for these hydrocarbons during day-time when OH radical concentration maximises. -The variability increases, likely resulting from fuel evaporation and combustion, is an effect that might occur mainly in large conurbation areas, with very tall buildings, which would allow accumulation of the emitted hydrocarbons along their streets (Tsai et al., 2006). As in the present work measurements have been undertaken both at a natural and at a rural site, which are located in large open areas, such phenomenon can not occur and hence our data support the statement of “distinct minimum during the warm season”, which is mainly attributed to photochemistry. About the i-butane/n-butane ratio -The authors admit that the sentence “Ěthis is clearly indicating the presence of Cl atoms in the area” is confusing and in the revised version is reformulated accordingly with the referee suggestion. This paragraph is mainly aimed to provide indirect evidence that our observations infer the existence of the Cl atoms and then to estimate their levels by using a more vigorous approach. -Rates of removal by OH radical and Cl atom for i-butane (kOH=2.19 x 10-12, kCl=1.43 x 10-10), n-butane (kOH=2.40 x 10-12, kCl=2.18 x 10-10) and propane (kOH=1.01 x 10-12, kCl=1.40Œ10-10), in units of cm3 molecule-1 s-1, suggest normally ratios of about 2:2:1 due to reaction with OH alone and approximately 1:2:1, respectively, due to reaction with Cl alone. Due to the differences in the hydrocarbon reactivity toward OH radical and Cl atom, examination of the i-butane/n-butane vs. n-butane distribution may indicate at a first insight the dominant acting radical chemistry, which in case of OH predominance would lead to a constant i-butane/n-butane ratio. Atmospheric dilution and mixing effect can be diminished by including in the analysis of a new hydrocarbon, in this case propane. Again if the hydrocarbon chemistry is driven only by OH, the ratio of i-butane/n-butane would remain constant with the increase in the i-butane/propane ratio, while a more predominant Cl chemistry would determine a constant i-butane/propane ratio with the increase in the i-butane/n-butane ratio.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Data in Fig. 4b shows that during high insolation period the i-butane/n-butane ratio varied between 0.3 (0.6) and 3.0 (ś0.45, 1 s; standard deviation), while the i-butane/propane ratio was in the range 0.3 and 0.8 (ś0.11). During low insolation period the i-butane/n-butane ratio (0.3 and 1.4, ś0.28), almost equalled that of the i-butane/n-propane (0.1 and 1.4, ś0.32).

Discussion on the possible influence of the data approaching LOD on the trend observed in Fig. 4 (Fig. 5 in the revised version of the manuscript) is in detail presented in the answer for Referee #2.

The observed increase in the i-butane/n-butane ratio at lower values of the i-butane/propane ratio (Fig. 4b) cannot be accounted only by the slight differences in the OH reaction rate coefficient for the butanes (Fig. 4(a, b)) and hence alternative hydrocarbon removal pathways might exist.

If the above statements are available than data presented in Fig. 4a,b shows that both natural and rural air masses are affected simultaneously by OH radical and Cl atom chemistry with distinct slopes depending on the available solar radiation intensity. -Although Cl atom presence in the troposphere of the investigated area is mainly indirectly inferred from hydrocarbon measurements, our hypothesis is supported by the data obtained applying Rudolph et al. (1997) and Singh et al. (1996) concepts, and measurements performed by using the aerosol filter pack technique to derive HCl concentration in the area. -However, hydrocarbon lifetime-variability relationship has also been investigated and similar results were obtained concerning the inferred Cl concentration. Moreover, data similar to that reported by Pszenny et al. (2007), in terms of high Cl atom level presence, were obtained. This part of the work is not here included as is subject to another paper dealing with hydrocarbon variability at various sites including urban, rural and natural. -Other approaches, as simple empirical models to fit observations of tetrachloroethene, ethane, ethyne and propane distribution over the Southern Ocean (Wingenter et al., 1999), or measurements of ethane and hydroxyl radical over the equatorial Pacific Ocean (Wingenter et al., 2005), were also used to

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

estimate the Cl atom levels in these areas.

The map A map included in the revised version indicates the location of the two sites investigated in the present study. The statement concerning possible local anthropogenic influences on higher values of the Cl atom at the rural site relies on the following observation: Cl in the area is related with the presence of HCl in the gas phase produced via displacement of NaCl by acidic constituents as H2SO4 and HNO3 through the following processes: NaCl + HNO3(g) = NaNO3 + HCl(g) 2NaCl + H2SO4(g) = Na2SO4 + 2HCl(g) The rural site is situated closer to the major urban area of the island and thus is more susceptible to the influence from the anthropogenic pollution sources. Indeed, the anthropogenic impact at this site has been seen by the mean of other pollution tracers as acetylene and black carbon (BC). More acidic anthropogenic constituents could contribute to an enhancement in the displacement mechanism of the Cl- to form HCl in the gas phase. Thus it is suspected that this mechanism should present some interest in order to be further investigated.

As we have earlier mentioned, an important work recently published by Pszenny et al. (2007) in J. Geophys. Res. reports similar conclusion with our study in terms of the presence of high Cl atom levels (similar to those estimated in the present work). In Pszenny et al. (2007), higher Cl levels are reported under more polluted air masses. This new reference has been added in the revised version of the manuscript as it seems to be very important for comparison purposes.

Other technical corrections are already implemented in the original text.

Indeed, as earlier mentioned, the aim of the present work is to provide, for the first time to our knowledge, information on the seasonal variation of OH and Cl radicals in a polluted marine site, by using well established methodologies. We feel that this result is of a great interest not only for the people working in the area but also for the scientific community.

References Apel, E.C., Calvert, J.G., and Fehsenfeld, F.C.: The non-methane hydrocarbon intercomparison experiment (NOMHICE): Tasks 1 and 2, J. Geophys. Res., 99, 16651-16664, 1994. Boissard, C. : Distributions tropospheriques globales des hydrocarbures legers: de l'experimentation a la mode1isation, PhD, Paris VII University, 1992. Boissard, C., Bonsang, B., Kanakidou, M., and Lambert, G.: TROPOZ II: Global distributions and budgets of methane and light hydrocarbons, J. Atmos. Chem., 25, 115-148, 1996. Bonsang, B., and Lambert, G.: Nonmethane hydrocarbons in an oceanic atmosphere, J. Atmos. Chem., 2, 257-271, 1985. Bonsang, B. and Kanakidou, M.: Non-methane hydrocarbon variability during the FIELDVOC'94 campaign in Portugal, Chemosphere - Global Change Science, 3, 259-273, 2001. Bonsang, B., Kanakidou, M., and Lambert, G.: Non methane hydrocarbons chemistry in the atmosphere of an equatorial forest: A case of indirect photochemical production of OH radicals, Geophys. Res. Lett., 14, 1250-1253, 1987. Bonsang, B., Kanakidou, M., Lambert, G., and Monfray, P.: The marine source of C2-C6 aliphatic hydrocarbons, J. Atmos. Chem., 6., 3-20, 1988. Durana, N., Navazo, M., Gomez, M.C., Alonos, L., Garcia, J.A., Ilardia, J.L., Gangoiti, G., and Iza, J.: Long term hourly measuements of 62 non-methane hydrocarbons in an urban area: Main results and contribution of non-traffic sources, Atmos. Environ., 40, 2860-2872, 2006. EURACHEM/CITAC Guide, Quantifying uncertainty in analytical measurements, Ellison, S.L.R., Rosslein, M., and Williams, A., eds., 2000. Hakola, H., Hellen, H., and Laurila, T.: Ten years of light hydrocarbons (C2-C6) concentration measurements in background air in Finland, Atmos. Environ., 40, 3621-3630, 2006. Hopkins, J.R., Lewis, A.C., and Seakins, P.W.: Analysis and applications of measurements of source dominated hydrocarbon concentrations from the PUMA campaigns in June/July 1999 and January/February 2000 at an urban background site in Birmingham, UK, Atmos. Environ., 39, 535-548, 2005. Kanakidou, M., Bonsang, B., Le Roulley, J.C., Lambert, G., Martin, D., and Sennequier, G.: Marine sources of atmospheric acetylene, Nature, 333, 51-52, 1988. Kanakidou, M, Bonsang, B., and Lambert, G.: Light hydrocarbons vertical profiles and fluxes in a French rural area, Atmos. Environ., 23, 921-927, 1989. Komenda, M., Parusel, E., Wedel, A., and Koppmann, R.: Measurements of biogenic VOC emissions: sampling, analysis and calibration, Atmos. Environ., 35, 2069-2080, 2001. Kouvarakis, G., Tsigaridis, K., Kanakidou M., and Mihalopoulos, N.: Temporal variations of surface regional background ozone over Crete island in the southeast Mediterranean, J. Geophys. Res., 105, 4399-4407, 2000. Liakakou, E.: Factors controlling the variability of NMHCS above the Eastern Mediterranean, PhD Thesis, University of Crete, 2007. Liakakou, E., Vrekoussis, M., Bonsang, B., Donousis, Ch., Kanakidou, M., and Mihalopoulos, N.: Isoprene above the Eastern Mediterranean: Seasonal variation and contribution to the oxidation capacity of the atmosphere, Atmos. Environ., 41, 1002-1010, 2007. Mihalopoulos, N., Stephanou, E., Kanakidou, M., Pilitsidis, S., and Bousquet, P.: Tropospheric aerosol ionic composition in the eastern Mediterranean region, Tellus, 49B, 314-326, 1997. Plass-Dulmer, C., Michl, K., Ruf, R., and Berresheim, H.: C2-C8 hydrocarbon measurement and quality control procedures at the Global Atmosphere Watch Observatory Hohenpeissnberg. J. Chrom. A, 953, 175-197, 2002. Putaud, J.P., Raes, F., Van Dingenen, R., Bruggemann, E., Facchini, M.C., Decesari, F., Fuzzi, S., Gehrig, R., Uglin, C.H., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Muller, K., Rodriguez, S.Q.S., Schneider, J., Spindler, G., ten Brink, H., Torseth, K., and Wiedensohler, A.: A European aerosol phenomenology. 2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, Atmos. Environ., 38, 2579-2595, 2004. Pszenny, A.A.P., Fischer, E.V., Russo, R.S., Sive, B.C., and Varner, R.K.: Estimates of Cl atom concentrations and hydrocarbon kinetic reactivity in surface air at Appledore Island, Maine (USA), during International Consortium for Atmospheric Research on Transport and Transformation/Chemistry of Halogens at the Isles of Shoals, J. Geophys. Res., 112, D10S13, doi:10.1029/2006JD007725, 2007. Read, K.A., Lewis, A.C., Salmon, R.A., Jones, A., and Bauguitte, S.: OH and halogen atom influence on the variability of non-methane hydrocarbons in the Antarctic Boundary Layer, Tellus, 59, 22-38, 2007. Rudolph, J., Ramacher, B., Plass-Dulmer, C., Muller, K.P., and Koppmann, R.: The indirect determination of chlorine atom concentration in the troposphere from changes in the patterns of non-methane hydrocarbons, Tellus, 49, 592-601, 1997. Singh, H.B., Gregory, G.L., Anderson, B., Browell, E., Sachse, G.W., Davis, D.D., Crawford, J., Bradshaw, J.D., Talbot, R., Blake, D.R., Thornton, D., Newell, R., and Merill, J.: Low ozone in the marine boundary layer of the tropical Pacific ocean: Photochemical loss, chlorine atoms, and entrainment, J. Geophys. Res., 101, 1907-1917, 1996. Steinbacher, M., Dommen, J., Ordonez, C., Reimann, S., Gruebler, F.C., Staehelin, J., and Prevor, A.S.H.: Volatile organic compounds in the Po Basin. Part A: Anthropogenic VOCS, J. Atmos. Chem. 51, 271-291, 2005. Tsai, W.Y., Chan, L.Y., Blake, D.R., and Chu, K.W.: Vehicular fuel composition and atmospheric emissions in South China: Hong Kong, Macau, Guangzhou, and Zhuhai, Atmos. Chem. Phys., 6, 3281-3288, 2006. Van Dingenen, R., Raes, F., Putaud, J.P., Baltensperger, U., Charron, A., Facchini, M.C., Decesari, S., Fuzzi, S., Gehrig, R., Hansson, H.G., Harrisonc, R.M., Uglin, C.H., Jones, A.M., Laj, P., Lorbeer, G., Maenhaut, W., Palmgren, F., Querol, X., Rodriguez, S., Schneider, J., ten Brink, H., Tunved, P., Torseth, K., Wehner, B., Weingartner, E., Wiedensohler, A., and Wahlin, P.: A European aerosol phenomenology. 1: physical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, Atmos. Environ., 38, 2561-2577, 2004. Vrekoussis, M., Kanakidou, M., Mihalopoulos, N., Crutzen, P.J., Lelieveld, J., Perner, D., and Berresheim, H.: Role of NO3 radicals in oxidation processes in the Eastern Mediterranean troposphere during the MINOS campaign, Atmos. Chem. Phys., 4, 169-182, 2004. Wingenter, O.W., Blake, D.R., Blake, N.J., Sive, B.C., Rowland, F.S., Atlas, E., and Flocke, F.: Tropospheric hydroxyl and atomic chlorine concentrations, and mixing timescales determined from hydrocarbon measuerments made over the Southern Ocean, J. Geophys. Res., 104, 21819-21828, 1999. Wingenter, O.W., Sive, B.C., Blake, N.J., Blake, D.R., and Rowland, F.S.: Atomic chlorine concentratios derived from ethane and hydroxyl measuremnts over the equatorial Pacific Ocean: Implication for dimethyl sulphide and bromine monoxide, J. Geophys. Res., 110, D20308, doi:10.1029/2005JD005875, 2005. Yang, K.L., Ting, C.C., Wang, J.L., Wingenter, O.W., and Chan, C.C.: Diurnal and seasonal cycles of ozone precursors observed from continuous measurement at an urban site in Taiwan, Atmos. Environ., 30, 2829-2838, 2005.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 6329, 2007.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper