Significant concentrations of nitryl chloride observed in rural continental Europe associated with the influence of sea salt chloride and anthropogenic emissions
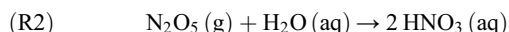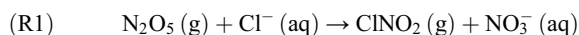
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[1] We present the first measurements of nitryl chloride ($ClNO_2$) over continental Europe. Significant quantities of $ClNO_2$, up to 800 pptv, were measured at a mountaintop field site in Hessen, southwest Germany. $ClNO_2$ was detected during the majority of nights between the 15th August and 16th September 2011, its largest mixing ratios being associated with air masses influenced by sea salt and anthropogenic NO_x emissions. $ClNO_2$ persisted in measurable quantities until early afternoons on days with low photolysis frequencies. As a consequence, early morning production rates of Cl atoms could significantly exceed the production of OH via ozone photolysis, likely leading to increased O_3 production. **Citation:** Phillips, G. J., M. J. Tang, J. Thieser, B. Brickwedde, G. Schuster, B. Bohn, J. Lelieveld, and J. N. Crowley (2012), Significant concentrations of nitryl chloride observed in rural continental Europe associated with the influence of sea salt chloride and anthropogenic emissions, *Geophys. Res. Lett.*, *39*, L10811, doi:10.1029/2012GL051912.

1. Introduction

[2] $ClNO_2$ is formed via the heterogeneous reaction of N_2O_5, a nocturnal NO_x reservoir, with particle Cl^- (R1) [*Finlayson-Pitts et al.*, 1989] which may compete with heterogeneous hydrolysis of N_2O_5 to form HNO_3 (R2):

$$(R1) \qquad N_2O_5\,(g) + Cl^-\,(aq) \rightarrow ClNO_2\,(g) + NO_3^-\,(aq)$$

$$(R2) \qquad N_2O_5\,(g) + H_2O\,(aq) \rightarrow 2\,HNO_3\,(aq)$$

[3] The formation of $ClNO_2$ thus depends on the Cl^- content of aerosol particles and their abundance [*Behnke et al.*, 1997; *Bertram and Thornton*, 2009; *George et al.*, 1994; *Roberts et al.*, 2009; *Schweitzer et al.*, 1998]. Factors controlling the mixing ratio of N_2O_5 (e.g., NO_2 and O_3 levels and the lifetime of NO_3) and the rate of uptake of N_2O_5 to aerosol (e.g., particle nitrate or organic content [*Bertram and Thornton*, 2009]) define the production rate of $ClNO_2$.

Nighttime losses of $ClNO_2$ are expected to be slow though some conversion to Cl_2 on acidic, chloride containing particles may take place [*Roberts et al.*, 2008].

[4] $ClNO_2$ is photolabile (noontime photolysis frequency typically 4×10^{-4} s^{-1}, a lifetime of $\sim$ 40 minutes) and can dissociate to form Cl and NO_2:

$$(R3) \qquad ClNO_2 + h\nu \rightarrow Cl + NO_2$$

In combination, reactions (R1) and (R3) represent a mechanism for the transformation of inorganic, particle-bound chloride into highly reactive chlorine atoms in the gas-phase and also reduce up to a factor of two the heterogeneous loss of NO_x via N_2O_5 uptake to particles.

[5] An important consequence of Cl atom formation is an enhancement of the oxidation rates of several VOCs leading to larger rates of regional photochemical O_3 formation, also favored by counteracting the reduction in nighttime NO_x loss [*Simon et al.*, 2009, 2010]. The importance of (R1) for the formation of reactive Cl sources in tropospheric chemistry was hypothesized by *Finlayson-Pitts et al.* [1989]. The importance of $ClNO_2$ in the ambient atmosphere was discovered by *Osthoff et al.* [2008] who measured more than 1 ppbv of $ClNO_2$ in the polluted marine air off the coast of Texas. Recently, two studies have underlined the global importance of $ClNO_2$ formation with the measurement of significant quantities of $ClNO_2$ over the urban North American continent far from the marine atmosphere, in Colorado, USA [*Thornton et al.*, 2010] and Calgary, Canada [*Mielke et al.*, 2011]; both studies suggest that an anthropogenic source of chloride is responsible for the formation of the urban continental $ClNO_2$ owing to the lack of marine influence in their measurements. These recent observations of an atomic chlorine source over the North American continent highlight the current lack of observations above the European continent and other polluted continental regions impacted by sources of particle chloride.

2. Site Location and Methods

[6] The measurements were made at the Taunus Observatory of the University of Frankfurt, located at 50.22°N, 8.45°E and 825 m above sea level at the summit of the "Kleiner Feldberg", a mountain in the Taunus range in South-western Germany. The semi-rural location is impacted by pollution from the densely populated Rhein-Main area (pop. 2 million) including an extensive motorway system and large cities such as Frankfurt (pop. 700 000, 30 km SE), Wiesbaden (pop. 300 000, 20 km SW) and Mainz (pop. 200 000, 25 km SSW). The area 50–100 km north of Kleiner

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Feldberg is lightly populated and devoid of major industry. The site has been described in detail by *Handisides* [2001] and *Crowley et al.* [2010]. In contrast to conditions reported in *Crowley et al.* [2010], during which air masses from continental E. Europe were sampled, our measurement period was mainly impacted by air masses originating from the NW and the SW. The nearest coastal regions are ~380 km to the North (North Sea) and 400 km to the Northwest (English Channel).

[7] Nitryl chloride was measured using iodide-ion chemical ionisation mass spectrometry (CIMS). The CIMS instrument was constructed by THS Instruments, Georgia, USA and is based on the CIMS technique described by *Slusher et al.* [2004] and *Zheng et al.* [2011], which has been previously used to measure ClNO$_2$ in the field [*Kercher et al.*, 2009; *Mielke et al.*, 2011; *Osthoff et al.*, 2008; *Thornton et al.*, 2010]. The air sample is drawn into the vacuum system via a pinhole into the ion-molecule reactor (IMR) region held at a pressure of 21 Torr. Iodide, generated by the irradiation of CH$_3$I, is introduced into the IMR in a stream of N$_2$ to ionize the sample. The ions are formed along the length of the flow tube and transmitted through an aperture to the collisional dissociation chamber for the removal of ion clusters. The ions are then guided via an octopole to mass selection in the quadrupole and detected at the channeltron. The instrument was optimised for the measurement of peroxycaboxylic nitric anhydrides (PANs) as part of the "Particles and radicals: diel observations of the impact of urban and biogenic emissions campaign" (PARADE) and a full description of the instrument and the gas and particle phase chemistry of reactive nitrogen at the site will be published when the full dataset is available (Phillips et al., manuscript in preparation, 2012). The detection of ClNO$_2$ was initially a secondary objective of the instrument deployment. ClNO$_2$ was monitored at I^{37}Cl$^-$ (m/z = 163.9, with a LOD (2σ) of 12 pptv) for the entire period with the addition of IClNO$_2^-$ (m/z = 207.9), with a LOD (2σ) of 3 pptv, from the 2/09/11, which is more specific and has a low background signal [*Osthoff et al.*, 2008]. The accuracy was estimated at 25%. The sample was drawn down a 3/8″ OD PFA tube 8 m in length at 20 lpm resulting in a residence time of 1 second. No indication of the production of ClNO$_2$ on the tubing walls was observed. The analytical signal was normalized using the primary ion signal, and the instrument sensitivity was determined post-campaign by the measurement of a ClNO$_2$ standard synthesized by passing Cl$_2$ over a mixture of NaNO$_2$ and NaCl crystals in a flow of humidified N$_2$. The concentration of the standard was determined using thermal-dissociation cavity ring-down absorption spectroscopy (TD-CRDS) in a similar manner to that described by *Thaler et al.* [2011]. A zero measurement, using a bypass with 25 cm of metal wool heated to 473 K, was made once an hour along with a standard addition for the measurements of PANs. N$_2$O$_5$ was measured using off-axis cavity ring-down (OA-CRD) described by *Schuster et al.* [2009] and *Crowley et al.* [2010]. Photolysis frequencies were determined by spectroradiometry [*Bohn et al.*, 2008] using molecular parameters from NASA/JPL 2011 [*Sander et al.*, 2011]. Temperature and relative humidity data were obtained from the Hessisches Landesamt für Umwelt und Geologie (HLUG) monitoring station at the measurement site.

[8] The HYSPLIT model [*Draxler and Hess*, 1998] was used to calculate 48 hour back-trajectories for the measurement period and these were classified by origin into five sectors. Forecast sea salt optical depth data at 550 nm wavelength, calculated using 24-hour forecast wind fields, were obtained from the EU FP7 Monitoring Atmospheric Composition and Climate (MACC) project, whose model construction and performance is described in *Benedetti et al.* [2009] and *Morcrette et al.* [2009].

3. Results and Discussions

[9] The time series of ClNO$_2$, N$_2$O$_5$ and sea salt optical depth are shown in Figure 1. There is large, night-to-night variability in the mixing ratios of ClNO$_2$ and N$_2$O$_5$ in addition to a large variable ratio between the two species in common with previous ambient measurements [e.g., *Mielke et al.*, 2011; *Osthoff et al.*, 2008; *Thornton et al.*, 2010]. N$_2$O$_5$ was not measured after the night of the 9th of September. The large variations in the ClNO$_2$-to-N$_2$O$_5$ ratio presumably reflect variable particle abundance and composition (chloride / water content) and the lifetime of N$_2$O$_5$ with respect to heterogeneous loss to particles. Whilst the calibrated signals at m/z = 163.9 and 207.9 are generally very similar, the ClNO$_2$ data obtained from the signal at m/z = 163.9 has a noticeably higher daytime background and the difference between the two signals, ClNO$_2$ (163.9) − ClNO$_2$ (207.9), during, e.g., the period 01/09 until the 05/09 displayed a diurnal profile with a maximum at 1400 hrs consistent with that expected from a photochemically generated species. It is highly probable that the daytime signal detected at 163.9 is due to a species other than ClNO$_2$, and assuming a similar sensitivity this would result in mixing ratios of over 100 pptv on several occasions. During the latter part of the campaign the signal from both m/z 163.9 and m/z 207.9 agree well during the nights where ClNO$_2$ production might be expected.

[10] The campaign can be separated meteorologically into three parts. The first period ("Continental") was changeable, with the majority of air sampled from the 15th to the 26th August having largely continental origin in the south to west wind sector. Although this period was impacted significantly by continental European NO$_x$ emissions resulting in high nighttime N$_2$O$_5$ mixing ratios on the nights 16–17th or 21–22nd, little or no ClNO$_2$ was detected. The influence of marine air masses during this period was also small as indicated by the small forecast sea salt optical depths compared with other periods in the campaign. The exception to this were two short periods when air was sampled originating from over the UK and the English Channel, both of which were marked by peak mixing ratios of 150 pptv on the night of the 16th/17th of August and 500 pptv on the night of the 19th/20th of August.

[11] The second part of the measurement period ("UK-Marine"), from the 26th August to the 5th September, began with a cold front moving over the measurement site from the west with an origin over the Atlantic. The relative humidity was 100% from the evening of the 26th until midday on the 27th. Initially, mixing ratios of N$_2$O$_5$ and ClNO$_2$ were near zero or low with peak ClNO$_2$ mixing ratios of 50 and 80 pptv on the nights of 27th/28th and 28th/29th, respectively, attributed to large loss rates of N$_2$O$_5$ in the rain and fog/low cloud at the measurement site. During the 29th August the air started to become influenced by the UK and the Benelux countries as indicated by the back-trajectories
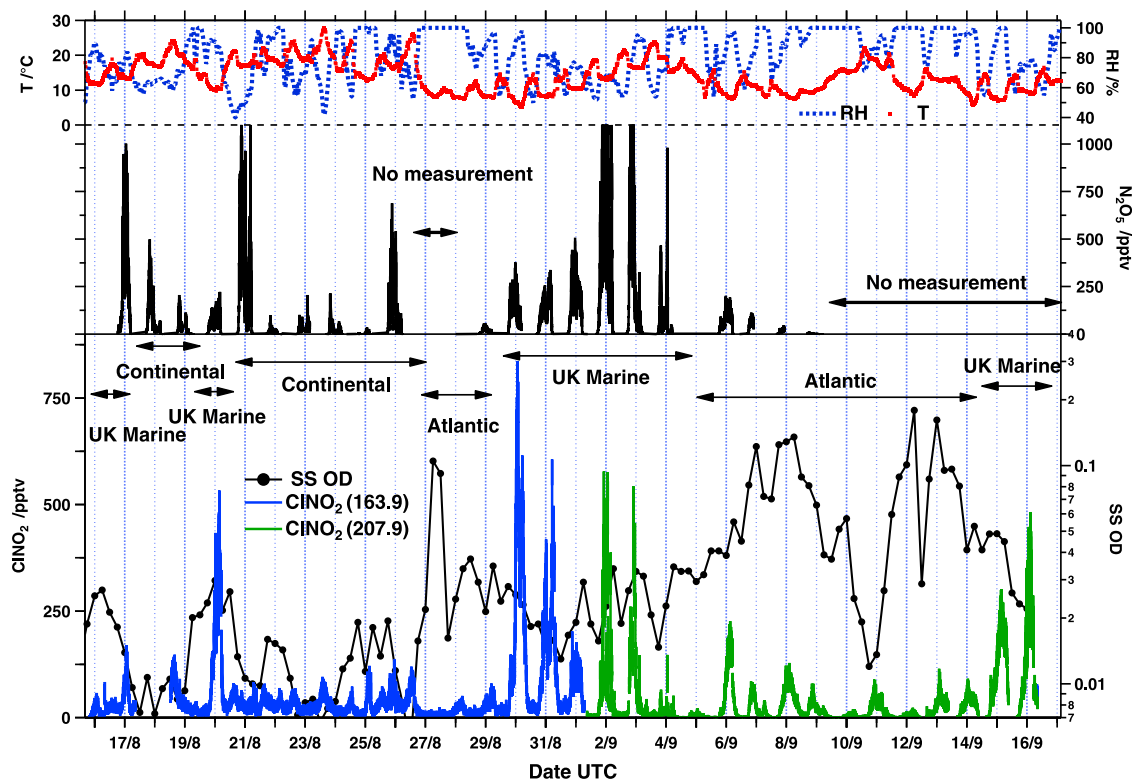
Figure 1. Time series of ClNO₂, N₂O₅ and ancillary measurements during the PARADE campaign. (top) The relative humidity (dashed line) and the temperature (red line). (middle) The mixing ratio of N₂O₅ (black line). Period where no measurements of N₂O₅ was made is indicated with an arrow. (bottom) The mixing ratios of ClNO₂ from mass-to-charge ratios 163.9 (blue line), until daytime on the 1st of September, and 207.9 (green line), from the 1st of September. 24 hour forecast sea salt optical depth (SSOD, black line with dots). Air mass back trajectory origins are indicated by the black arrows.

and increase in N_2O_5 mixing ratios over the next few nights. The increase in the forecast sea salt optical depth was maintained throughout the period from the passing of the front on the 26th August and the largest mixing ratios, 800 pptv, of $ClNO_2$ were observed. From the 1st of September the air mass origin moved closer to the measurement site with the 48-hour back trajectory starting over the European continent within 400 km of the measurement site on the nights of the 2nd and 3rd of September. Very large mixing ratios of N_2O_5 were observed on these two nights coinciding with large mixing ratios of $ClNO_2$ of up to 750 pptv.

[12] The passage of another weather front on the 5th of September marks the final part of the measurement period ("Atlantic"), which was characterized by westerly air masses with an Atlantic origin. The largest sea salt optical depths are predicted for this period of the campaign. $ClNO_2$ was detected every night until the end of the measurement period, from the 5th to the 16th of September. The mixing ratios varied significantly from night to night during this period, with largest observed on the last three nights when the air masses began to be influenced by the UK.

[13] Different chemical regimes of $ClNO_2$ production can be observed in this dataset. Figure 2 shows six cases of nocturnal $ClNO_2$ production with differing conditions. The $ClNO_2$-to-N_2O_5 ratio varied by over an order of magnitude from ∼3 (Figure 2a, 03:30 UTC) to ∼0.2 (Figure 2d, 22:30 UTC). Similar variability in $ClNO_2$-to-N_2O_5 ratios was observed by *Thornton et al.* [2010] in the continental

USA and may be partially attributed to availability of particle Cl^- with marine air masses (see above).

[14] The large difference in $ClNO_2$ mixing ratios from continental air masses and those with large sea-salt optical depths suggests that the Kleiner Feldberg measurement site is significantly impacted by air masses with a marine origin. Owing to the lack of total particulate ionic composition measurements we have however only indirect evidence as to the source of the Cl^- responsible for the formation of $ClNO_2$. Evidence for significant influence of sea salt in this region, when the prevailing wind was from the NE or NW, was reported by *Vester et al.* [2007] who found that aged sea salt accounted up to 75% of the super-micron particles sampled during some periods at a location 30 km SW of our measurement site. *Manders et al.* [2010] reported sea salt concentrations over the European continent, and found concentrations of between 2 and 5 $\mu g\ m^{-3}$ up to 300 km from the coast. *Tsyro et al.* [2011] report sea salt data from Melpitz, Germany (51.53°N, 12.93°E): concentrations of up to 2 $\mu g\ m^{-3}$ Na in PM10 were observed, with the highest sea salt concentrations occurring in air arriving from the Atlantic. Back trajectories indicate that 25 of the 33 campaign nights during which $ClNO_2$ was monitored, were influenced by marine environments (Atlantic, Mediterranean or English Channel) within the previous 48 hours. During transport from the coastal areas over polluted regions, sea salt can be depleted in chloride, which will transfer to the gas-phase either directly or as HCl through secondary reactions.
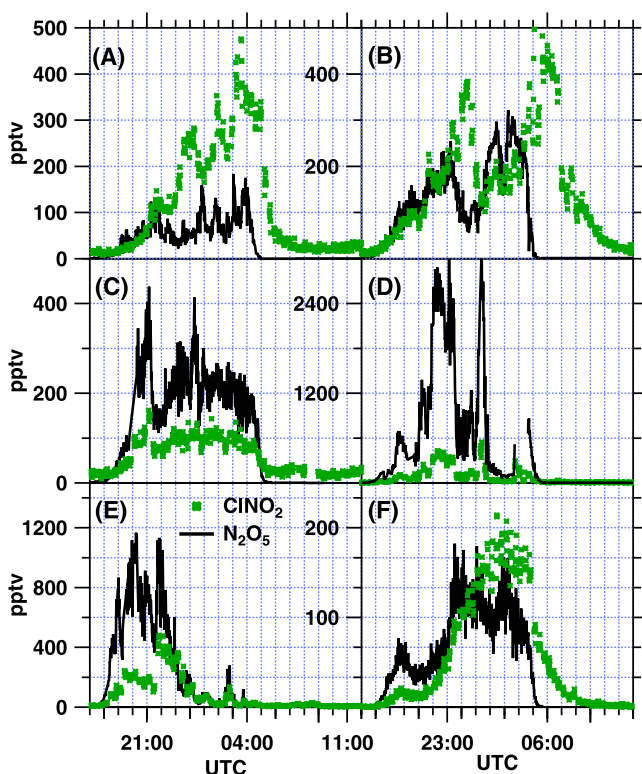
Figure 2. Six cases of nocturnal ClNO$_2$ production during the measurement period (ClNO$_2$ - stars, N$_2$O$_5$ - line). (a) 20th August; air masses originating over the English Channel. (b–e) 31st August to 3rd September showing day-to-day change in ClNO$_2$-to-N$_2$O$_5$ ratio in air originating over the UK. (f) 6th September; air originating over the Atlantic with high marine influence as indicated by high forecast sea salt optical depths.

O$_3$ photolysis is given by $R_{OH} = 2J(O^1D)[O_3] \, k_{H2O}[H_2O]/ (k_{H2O}[H_2O] + k_{N2}[N_2] + k_{O2}[O_2])$. As an example, Figure 3 shows the radical production rates for Cl and OH, via O$_3$ photolysis, on the morning of the 30th August using measurements of O$_3$, relative humidity, J_{ClNO2} and J_{O1D}, and the literature values for the rate coefficients for reaction of O(^{1}D) with H$_2$O, N$_2$ and O$_2$. From before sunrise, at around 04:45 UTC, until approximately 07:30 UTC, the production of Cl was larger than the production of OH from the photolysis of O$_3$ ($\approx$25 ppbv) with a sunrise production rate ratio of 10:1, decreasing to 1:1 at 07:30 UTC. More recent temperature-dependent measurements of ClNO$_2$ absorption cross sections by *Ghosh et al.* [2012] result in a ~30% decrease in the photolysis rate when compared to the current NASA/JPL recommendation, which translates into a comparable decrease in the Cl production rate. However, Cl production remains relatively important into the first 2–3 hours of the morning. Whilst a more detailed analysis of ClNO$_2$ at the Kleiner Feldberg awaits the availability of further PARADE datasets, it is clear that its observation has important repercussions for early morning photochemistry.

4. Conclusions

[17] The presence of significant quantities of nocturnal ClNO$_2$ over the Western European continent during August–September 2011 was the norm rather than the exception. The continental ClNO$_2$ during the measurement period most likely owes its presence to the interaction of anthropogenic NO$_y$ and marine sources of particle Cl$^-$, demonstrating the importance of the marine environment to chemistry above the European continent in particular to the chemistry of reactive nitrogen. In the early morning with significant concentrations of ClNO$_2$, the production rate of the Cl atoms exceeds the production of OH via O$_3$ photolysis for 2 to 3 hours after sunrise. Sea salt is often detected over the

This can then partition between the particle and gas phases so that, although originally of marine origin, the particulate chloride driving the formation of ClNO$_2$ must not necessarily be associated with coarse mode, sodium containing particles.
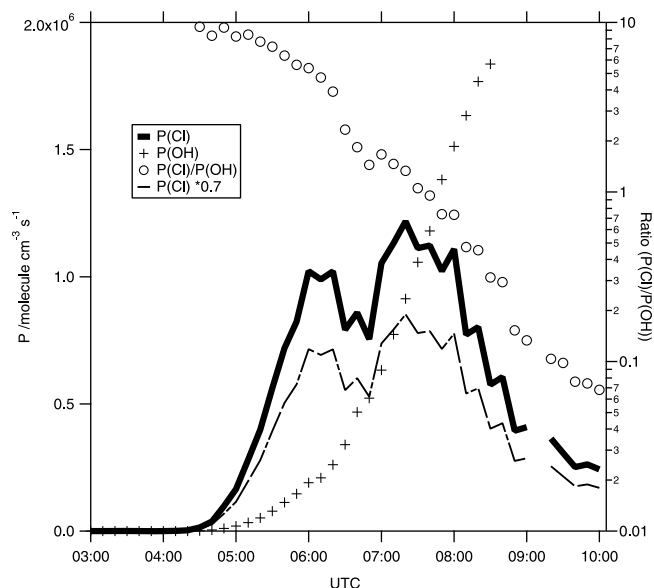
[15] Previous reports of continental ClNO$_2$ over North America hypothesize that the source of Cl is predominantly anthropogenic due to the lack of marine back-trajectory origin [*Mielke et al.*, 2011; *Thornton et al.*, 2010]. However, there are several indications that this is not the case in our dataset. From the 21st to 26th of August, air mass back trajectories and forecast MACC sea salt optical depth indicate little or no marine influence. This period of time was characterized by some of the highest NO$_x$ during the campaign and therefore one might expect the presence of anthropogenic chlorine. However, despite the presence of abundant N$_2$O$_5$, during these periods we observe little or no ClNO$_2$. Although we are unable to rule out a contribution of anthropogenic Cl$^-$ to the ClNO$_2$ budget, these data are more consistent with the majority of Cl$^-$ being of marine origin.

[16] The impact of the formation and daytime photolysis of ClNO$_2$ at this (and any other) site will be a Cl atom induced increase in the rate of oxidation of VOCs. A comparison of the radical production rates may be made, with Cl atom production from ClNO$_2$ photolysis given by $R_{Cl} = J_{ClNO2}[ClNO_2]$, and the production rate of OH from

Figure 3. Production rates of Cl atom via photolysis of ClNO$_2$ (black line-NASA/JPL 2011 and black dashed line-30% decrease), the production rate of OH via photolysis of O$_3$ (crosses) and the ratio of the radical production rates (open circles) for the morning of the 30th August.

European continent [e.g., *Manders et al.*, 2010; *Vester et al.*, 2007] and it can be expected that the formation of ClNO$_2$ is a common phenomenon and likely an important source of active halogens and thus enhances VOC oxidation and ozone formation rates over Western Europe.

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