In situ quantification of CH4 bubbling events from a peat soil using a new infrared laser spectrometer

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Abstract

Purpose CH_4 emissions from peatlands are space- and time-dependent. The variety of efflux routes contributes to these variabilities. CH_4 bubbling remains difficult to investigate since it occurs on a timescale of seconds. The aims of this study were to use for the first time the recently built infrared high resolution spectrometer, SPIRIT (SPectrometre Infra-Rouge *In situ* Troposphérique), to (1) measure *in situ* CH_4 fluxes in natural and artificial peatland plot, (2) observe online bubbling events with quantification of CH_4 emission fluxes corresponding to this very sudden degassing event.

Material and methods The closed dynamic chamber method was used and the gas concentration was measured every 1.5 seconds. Emission fluxes were calculated by the accumulation rate of CH_4 against time. Measurements were undertaken during daytime in March 2009 and during day- and nighttime in May 2009, in *Sphagnum* and *Betula plots*, and in a wet artificially bared peat area with *Eriophorum vaginatum*.

Results and discussion The results show that the CH_4 emissions estimated with the SPIRIT are consistent with those already published. The high emissions, both through diffusion and bubbling in the *Eriophorum* plot, were on the same order as the emissions estimated in natural shallow pools. During daytime, CH_4 bubbling was higher in May (54.7% of the total emission) than in March (40.7%) probably because of increased CH_4 production and accumulation in peat. In May, bubbling was higher at nighttime (65.5%) than in daytime (54.7%). This has an important implication for carbon budget assessment in peatlands.

Conclusions The recently built infrared spectrometer, SPIRIT, was able to reliably measure CH_4 fluxes and quantify CH_4 flux during the degassing of bubbles. The emissions obtained are in agreement with previously published data using other measurement techniques. The results of this preliminary work highlight (1) the importance of shallow pools in peatland CH_4 emissions, (2) the sensitivity of such fluxes to atmospheric pressure, a relation that has not been fully investigated or taken into account in assessing peatland carbon balance.

Keywords CH_4 efflux pathways • Carbon cycle • Methanogenesis • La Guette peatland • Infrared quantum cascade laser spectrometry

1 Introduction

CH_4 emission through bubbling has been recognized to be a significant route of CH_4 export from peatland to the atmosphere (e.g., Fechner-Levy and Hemond 1996; Christensen et al. 2003; Tokida et al. 2007). However, the closed static chamber technique coupled to gas chromatography often used to derive flux emissions of CH_4 is not sufficiently time resolution efficient to extract or even to observe bubbling events since they occur on a timescale of seconds. Tokida et al. (2007) suggested that this technique underestimates CH_4 flux because the assumptions behind the calculations require the rejection of apparently outlying data originating from bubbling events. Christensen et al. (2003) and Ström et al. (2005), using a photo acoustic multigas analyser, measured CH_4 emissions from peat cores in the laboratory every two minutes. They were able to assess the proportion of CH_4 emitted as bubbles in a range of different vegetations and sites. They used a statistical technique that highlighted outliers which they then assimilated to a bubbling event. This time resolution makes impossible the accurate identification and quantification of bubbling events that occur on a shorter time scale, i.e., seconds. What they identified as diffusive CH_4 emissions may contain few bubble events and their bubbling

events may contain diffusive episodes. Furthermore, they studied CH_4 emissions in laboratory conditions where processes may be quite different from in the field. Schrier-Ujil et al. (2010) used the same instrument in the field with a measurement every one minute. To estimate the fluxes, they calculated the linear regression of the curves with only 5 points, which made impossible the detection of bubbling events. SPIRIT (SPectrometre Infra-Rouge *In situ* Troposphérique), a new portable infrared laser high resolution spectrometer, is able to measure CH_4 concentration in the air every 1.5 seconds. Potentially, SPIRIT allows 1) *in situ* high precision CH_4 flux emission measurements in a few minutes or less with the closed chamber method and 2) the visualization and quantification of individual bubbling events. This paper reports the first results confirming the capability of SPIRIT to accurately estimate CH_4 flux from a peatland and to distinguish emission through diffusion from bubbling.

2 Materials and methods

The site studied is La Guette peatland, located near Neuvy-sur-Barangeon (Cher, Sologne) in the French "Région Centre" (altitude: 154m, N: 47°19', E: 2°16). It is a transitional fen (pH about 4-4.5) colonised by *Molina caerulea* and *Betula spp* (*Betula verrucosa* and *Betula pubescens*). The dominant *Sphagnum* species are *Sphagnum cuspidatum* and *Sphagnum rubellum* (Gogo et al. 2010). *In situ* measurements were carried out on the 19th of March 2009 during daytime (afternoon) and on the 26th of May during daytime and nighttime (27th of May). CH_4 emissions were measured in 3 sampling plots representing different vegetation (*Sphagnum cuspidatum*, *Betula* spp. and *Eriophorum vaginatum*) on the 19th of March 2009 and in the *Eriophorum* plot on the 26th and 27th of May 2009. The Sphagnum cuspidatum and the Betula plots are considered to represent natural, intact and typical peatland vegetation, whereas the *Eriophorum* plot initially corresponded to a bare peat area created as management works to renew the ecosystem and maintain biodiversity, which was later colonised by *Eriophorum vaginatum*.

SPIRIT is a portable infrared laser absorption spectrometer designed and built in our laboratory using a patented long path optical cell and a tunable Quantum Cascade Laser (Robert 2007). This instrument has been designed, based on our experience on the balloon-borne instrument SPIRALE operating with six lead-salt diode lasers simultaneously (Moreau et al. 2005). The latter has led to accurate data for chemistry and dynamics studies of the atmosphere (see e.g., Huret et al. 2006; Pirre et al. 2008; Mébarki et al. 2010) as well as for validation of satellite instruments such as Envisat MIPAS and GOMOS, ACE-SCISAT FTS, Odin SMR and Aura-MLS (see eg, Renard et al. 2008; Mébarki et al. 2010). The description of SPIRIT and of the process to derive CH_4 concentrations in the atmosphere are given in full detail elsewhere (Joly et al. 2008; Guimbaud et al. submitted). The CH_4 ro-vibrational line at 1270.78503 cm^{-1} was used (Rothman et al. 2005). A sampled volume rate (from 1 to 3 STP dm^3 min^{-1}) from SPIRIT is maintained in order to keep a short delay between sampling and analysis. The concentration precision, given by the precision on the absorption measurement and by the measured sensitivity to the concentration variation, was demonstrated to be better than 0.2% for a response time of 1.5 s (Guimbaud et al., submitted). For gas flux measurements, chamber method is preferred to micrometeorological methods (Hendriks et al., 2010) because emissions are studied at the scale of the vegetation type (1 m^2). The optical cell of SPIRIT was connected to a dynamic closed chamber meaning that the headspace chamber air is sampled from and re-injected to the chamber and passing through the SPIRIT optical cell. Permanent PVC cylinder collars (internal diameter = 30 cm) were sunk into the soil and emerging at 10 cm

above the *Sphagnum* capitulum, few days before measurments. In each plot, CH_4 fluxes are inferred from the slope of the stabilized linear increase of CH_4 concentration with time (from 3 to 10 minutes period), usually starting from the visible linear increase after sealing a 29 cm height chamber on the collar. A small fan was installed on top of the chamber to homogenize the inside air as recommended for high chambers (Rochette and Eriksen-Hamel, 2008). The flux of CH_4 per surface unit F^S (molecule m^{-2} s^{-1}) is given by Eq1.:

$$F^S = (P/k_bT) \,.\, h \,.\, (dX/dt) \qquad (1)$$

where P is the pressure in the chamber (Pa), k_B the Boltzmann constant (1.381×10^{-23} J K^{-1}), T the absolute temperature (K), h the mean height of the chamber above the soil surface (m) which is more precisely the volume of the closed loop to the surface ratio of the soil emitter, X the volume mixing ratio of CH_4 in the chamber (unit-less), dX/dt the rate of accumulation of CH_4 in the chamber (s^{-1}).

dX/dt is usually calculated using the linear regression method (Kroon et al., 2008) because no significant difference is observed compared to the slope intercept method or to the exponential regression method for the short integration period typically used to derive the flux unless flux attenuation occurs due to strong bubble events leading to very high level of CH_4 concentrations in the headspace of the chamber. In the later case, *dX/dt* is calculated using the exponential regression method given by Kroon et al. (2008). Care is taken to avoid known chamber artefacts as described by Davidson et al. (2002), which may affect the natural emission such as (i) pressure changes during chamber enclosure, (ii) inside and outside chamber pressures drift during accumulation, or (iii) alteration of the natural concentration gradient within the soil (or within the water table) due to the concentration rise in the headspace of the chamber. To avoid these respective artefacts, (i) the top of the chamber is connected to a wide outlet exit line open to the outside air and closed few seconds after enclosure (ii) the pressures inside and outside the chamber are continuously checked during accumulation with a manometer; the stability of pressures and the pressure differential are kept below 0.1 hPa, thanks to a vent located on top of the chamber as recommended by Davidson et al. (2002) and Hutchinson and Livingston (2001) and (iii) the flux measurement integration period was kept sufficiently short (from 5 to 20 minutes). Such artefacts can be observable on line due to the high frequency (0.7 Hz) of the concentration measurement. The flux detection limit for CH_4 is 1.7×10^{-2} mg C-CH_4 m^{-2} h^{-1}, with a precision better than 1% above 10 times the detection limit (calculated from the *dX/dt* linear regression for a single plot) (Guimbaud et al., submitted). The largest global uncertainty on individual flux is 10%, due to the uncertainty on the volume of the chamber (<8%, because of the vegetation present inside) from which the mean height is derived and due to the absolute accuracy on concentrations (<6%).

When CH_4 accumulation is measured with a closed chamber, bubbling of CH_4 is a sudden event causing the breakdown of the diffusion slope. In order to separate bubbling events from the diffusion process of CH_4 emission, the differences in CH_4 concentration at times t_i and $t_{(i-1)}$ were calculated (Fig. 1). The flat background corresponds to emission through diffusion and plant-transport, whereas spikes reflect bubbles and can be seen as outliers compared to the background line. These outliers were identified using plots of measured versus normal theoretical values (Quinn and Keough 2002) and the bubble event was clearly identified. The bubble contribution (Table 1) corresponds to the total amount of CH_4 released through bubbling divided by the entire time of the flux measurements, which gives the contribution of bubbling to the total CH_4 emission (Christensen et al. 2003). The instantaneous emissions (Table 2) correspond to the amount of CH_4 released during a single bubbling event divided by the time of this single event.

3 Results and discussion

In March, measurements in the *Sphagnum cuspidatum* and *Betula* plots were linear when no chamber artefacts occurs (more than 80% of the case). The slope was calculated using the linear regression of the curve (Fig. 2ab). In contrary, the level of CH_4 concentrations reached in the *Eriophorum* plot were much higher (5 to 25 ppm; Fig. 3) due to the presence of bubbling events in comparison to *Sphagnum cuspidatum* and *Betula* plots (2.5 ppm; Fig. 2). Thus, possible inhibition of the natural flux may occur during accumulation of CH_4 in the headspace of the chamber for *Eriophorum* plots. To test such an effect, the diffusive flux was calculated using both the linear and the exponential method (Table 2). The data corresponding to bubbles were removed and the time and the concentrations were adjusted to obtain a continuous curve to which was fitted the linear and the exponential model. The results showed that the March diffusive flux, with lower concentration than in May, was best described by the linear method, whereas the May fluxes (both day- and nighttime), with the highest level of CH_4 concentration were best described by the exponential method. This suggests that inhibition in high level of CH_4 concentration (>7 ppm) does occur. These results show that the SPIRIT is able (i) to measure CH_4 fluxes in different types of vegetation with different efflux pathway (diffusion-plant transport and bubbling) and (ii) to detect and record inhibition effect and apply the most efficient slope calculation method.

The values of CH_4 emissions measured in la Guette peatland are in the range of previously published data (e.g., Hamilton et al. 1994; Christensen et al. 2003; Pelletier et al. 2007; McEnroe et al. 2009; Fig.2, Table 1). CH_4 emission was lower for *Betula*, where the water table was lower (~-7.5 cm below surface), than for *Sphagnum cuspidatum*, where the water table was higher (~-5.5 cm below surface) (Fig.2). Although these data were obtained only on one date, they are in agreement with previous works demonstrating the relationship of CH_4 emissions and water table depth (i.e. Dinsmore, 2009). Anaerobic conditions of hummock favour methanotrophy and therefore reduce the amount of CH_4 emitted to the atmosphere. In the *Eriophorum* plot, the wettest of all plots, the high emissions in May fall within the upper range of reported values for CH_4 (McEnroe et al., 2009). The CH_4 emissions were measured in an artificial pool created in 2002 by the manager of the site as a way to renew the vegetation of this invaded peatland. In such wet plot, ebullition is suspected to be a major route of CH4 efflux to the atmosphere (Hendricks et al, 2010).

With SPIRIT, bubble events were clearly distinguished from diffusive phases and both phenomena were precisely quantified (see Figs. 1 and 3, Table 2). Although bubbles are very sudden, they can be the major route of CH_4 flux to the atmosphere (McEnroe et al. 2009). The contribution of *in situ* bubbling and instantaneous emissions fall within the range of those estimated in the laboratory by Christensen et al. (2003; Table 1), who measured instantaneous CH_4 emissions up to 1000 mg CH_4-C m^{-2} h^{-1}. In a Canadian peatland, Pelletier et al. (2007) measured CH_4 emissions as high as 250 mg CH_4-C m^{-2} h^{-1} with the closed chamber technique and using gas chromatography (one sample every 15 minutes for 1 hour). Although this method is less efficient in detecting sudden bubbling events, their high emission values probably reflect frequent bubbling events, similar in magnitude to our results, occurring between diffusion phases.

Both bubbling and diffusion were lower in March than in May (Fig. 3; Table 2). In May, when the conditions are more favourable for methanogenesis (higher temperature, better carbon source through increased primary production), more CH_4 is produced and therefore more CH_4 is emitted than in March (Avery et al. 2003;

Dinsmore et al. 2009). Furthermore, as the temperature is higher, gases are less soluble and CH_4 via bubbling and diffusion may be released faster than earlier in the season (Fechner-Levy and Hemond 1996; Comas et al. 2008).

In May, emissions of CH_4 from bubbles were higher than diffusion during nighttime compared to daytime (see Table 1). The atmospheric pressure was lower during the day than during the night (1004.2 hPa and 1011.3 hPa respectively). This is in apparent contradiction with previous work which suggested that decreasing atmospheric pressure may favour ebullition (Fechner-Levy and Hemond 1996; Tokida et al. 2007). Further studies are required to assess the relationship between CH_4 emission through bubbling and atmospheric pressure variation.

In La Guette peatland, SPIRIT measurements in *Sphagnum* and *Betula* plots did not show any bubbling events (Fig. 2). Bubbling depends on CH_4 concentration in pore water. The emission through vascular plants can reduce the CH_4 dissolved in water and thus prevent the formation of bubbles. The biomass in the *Eriophorum* plot was low (few individuals were present and covered no more than 20% of the sampling plot). If the biomass increases, then emission through bubbles may decrease. As the plant biomass was low, the clogging of bubbles in porous peat materials may explain the observation, as the fibrous nature of peat restrains bubbling (Kellner et al. 2004). This result suggests that the sensitivity to atmospheric pressure variations may be higher in open water sites than in vegetated sites. This supports the suggestions by Tokida et al. (2007) that CH_4 ebullition in specific areas of peatlands, namely the wettest areas, is a major route for CH_4 emissions. Therefore, measurements of CH_4 fluxes that did not take this route into account would greatly underestimate CH_4 emissions.

In conclusion, the results of this article suggest that more attention needs to be paid to CH_4 emissions through bubbles in wet areas such as natural pools or artificial bare peat during both daytime and nighttime, in order to achieve more accurate estimations of CH_4 flux at the ecosystem level. The characteristics and the proven *in situ* effectiveness of SPIRIT would allow the investigation of the relationship between *in situ* CH_4 flux and atmospheric pressure.

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Table captions

Table 1 Total CH_4 emissions in la Guette peatland, contributions of the different pathways to the total (mg CH_4-C $m^{-2}h^{-1}$) and percentage of CH_4 emitted through bubbles. Comparison with Christensen et al. (2003)

Table 2 Comparison between linear and exponential method in calculating the slope of CH_4 concentration increase within the chamber in March (daytime) and May (day- and nighttime)

Figure captions

Fig. 1 Difference over time (Universal Time: UT) in CH_4 concentration ($t_i - t_{(i-1)}$) showing bubbling events (arrows) during diffusive background (May – daytime)

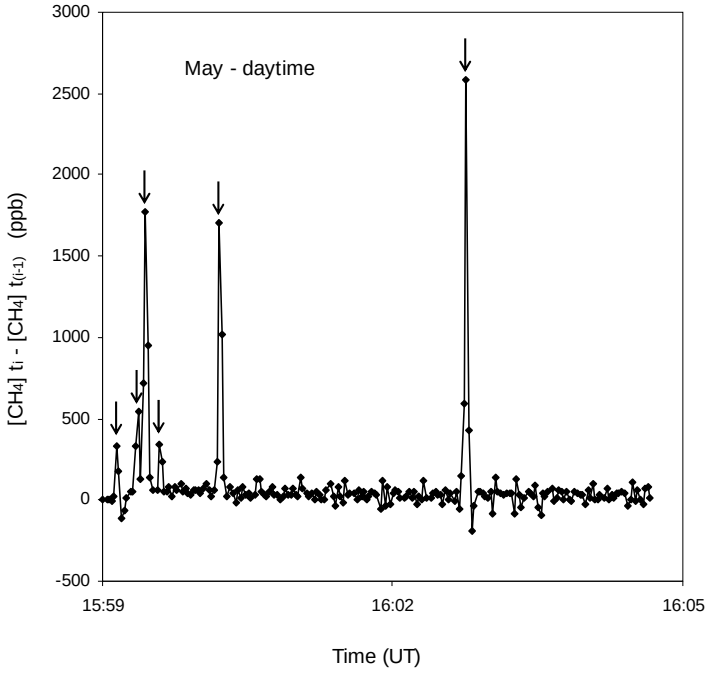
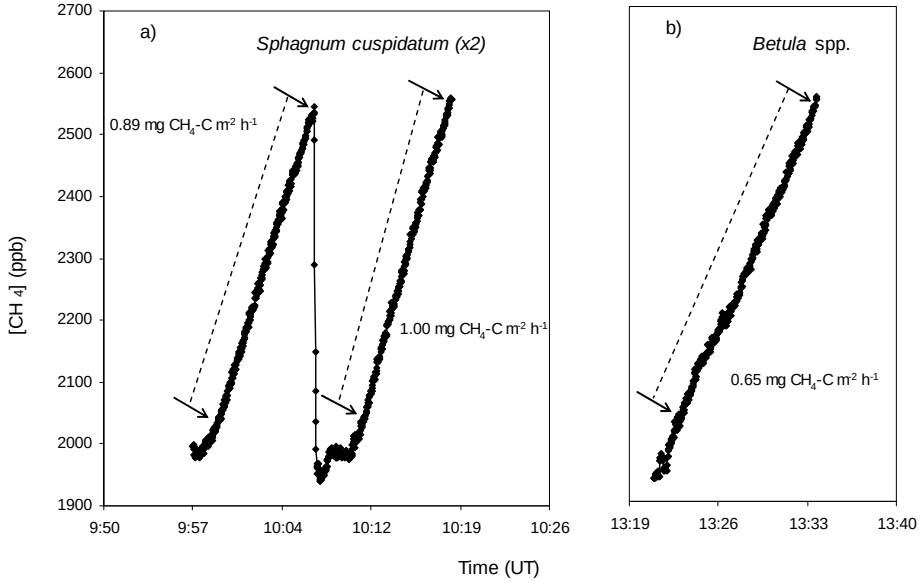


Fig. 2 Examples of CH_4 accumulation over time (Universal Time: UT) in ppb in the closed chamber in March daytime: in a *Sphagnum cuspidatum* plot (a) and in a *Betula* spp plot (b) in la Guette peatland. The data between the two arrows are used in the calculation of the fluxes. The two measurements in the same *S. cuspidatum* plot show a good repeatability. No bubbles were observed.



Fig; 3 CH_4 accumulation over time (Universal Time: UT) in ppb in the closed chamber in March daytime, May daytime and May nighttime. The arrows correspond to detected bubbling events. Note that in comparison with Figs 3b and 3c, in Fig. 3a the scale of the X axis is about 4 times longer and the scale of the Y axis is 3 times lower.

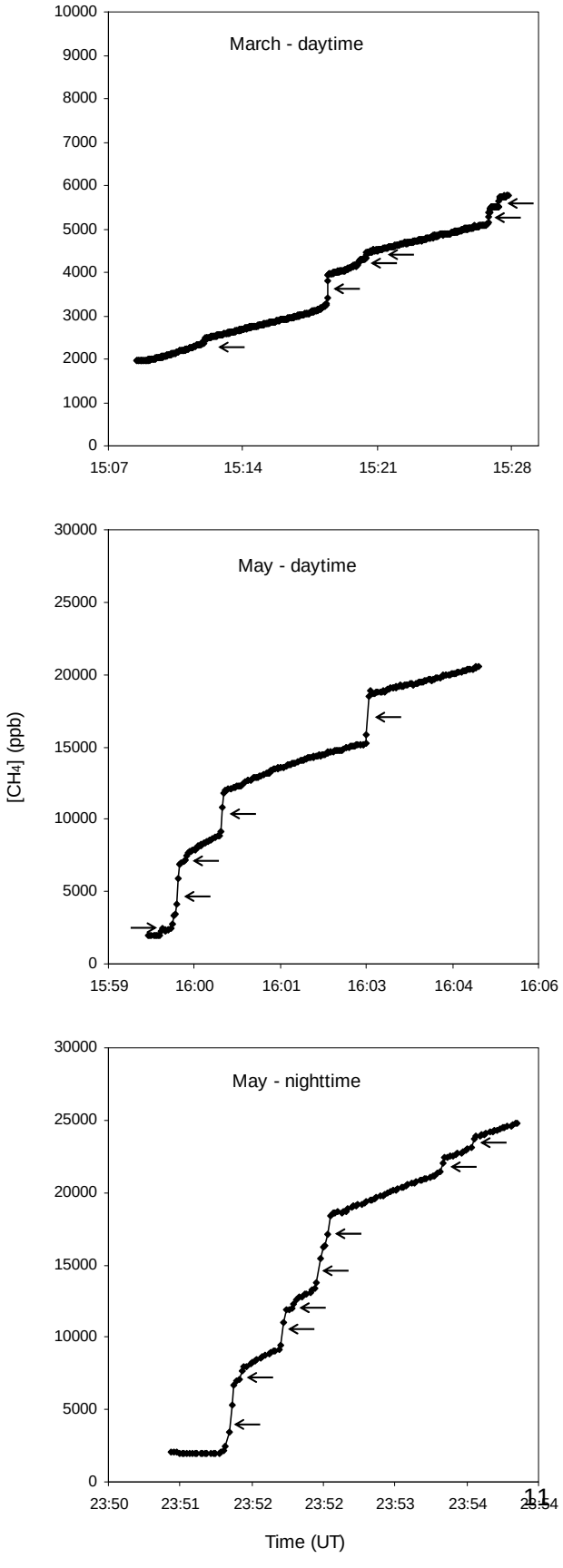


Table 1

	this study			Christensen et al (2003)			
	March 2009 - daytime	May 2009 - daytime	May 2009 - nighttime	Holmeja	Kopparås 1	Kopparås 2	Stordalen
Total emission	2.8	44.7	104	24.6	9.2	5.9	12.6
Diffusion contribution	1.7	20.3	34.7	17.5	4.5	4.4	10.4
Bubble contribution	1.1	24.5	68.9	7.1	4.7	1.5	2.1
% of CH_4 emitted as bubbles	40.7	54.7	66.5	28.8	51.5	25.8	17.0

Table 2

	Method	R^2	dC/dt (ppb s^{-1})
March - daytime	Linear	99.7	1.74
	Exponential	99.5	1.89
May - daytime	Linear	97.9	18.5
	Exponential	99.8	31.5
May - nighttime	Linear	99.0	53.1
	Exponential	99.3	67.0