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# AUTOMATED DETERMINATION OF MONOTERPENES IN A FORESTED AREA

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We have developed an automated analytical device, equipped with a preconcentration/thermodesorption module, in order to monitor natural hydrocarbons that occur in the atmosphere. The objectives of this study were to test the performances of the automated device on a Bavarian experimental forested site, and to determine the diurnal variation in atmospheric concentration of  $\alpha$ - and  $\beta$ -pinene at 2 and 21 m. The terpene concentrations ranged between 6 pptV ( $36 \text{ ng m}^{-3}$ ) and 216 pptV ( $1300 \text{ ng m}^{-3}$ ).

KEY WORDS: Monoterpenes, terpene concentration, automatic analysis, atmosphere, *Picea abies* (L.) Karst, Bavarian forest.

## INTRODUCTION

In a previous paper<sup>1</sup>, we have focused on the implication of airborne organic compounds of natural origin in a variety of physical and chemical atmospheric processes.

Amongst trace compounds resulting from natural emissions, isoprene and the principal monoterpenes ( $\alpha$ - and  $\beta$ -pinene,  $\Delta^3$ -carene, limonene) are expected to play an important role at the tropospheric level on account of their high reactivity and of the importance of the corresponding vegetal sources<sup>2-4</sup>. These hydrocarbons are prone to modify the  $\text{NO}_2$ - $\text{O}_3$ -NO cycle that governs the photochemical formation of ozone and its depletion. They are converted into oxygenated species (peroxides, aldehydes, ketones, acids) via ozonolysis, or by interaction with  $\text{O}^\bullet$ ,  $\text{OH}^\bullet$  and  $\text{NO}_3^\bullet$  radicals<sup>5-10</sup>. They also act as precursors to nucleation germs and aerosols<sup>11-14</sup>. The derivatives formed throughout the above mentioned processes (radicals, oxidants, acids, etc.) are often more aggressive toward the biosphere than the parent species<sup>21</sup>.

Mathematical models have been designed in order to evaluate the implication of trace atmospheric constituents in the complicated atmospheric processes. However, such models have to be validated by field and laboratory experiments. There are few models taking into

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account biogenic hydrocarbons, e.g., those of Lloyd *et al.*<sup>15</sup>, Trainer *et al.*<sup>16</sup>, Lübker and Schopp<sup>17</sup>, Novak and Regan<sup>18</sup>, Pierce *et al.*<sup>19</sup>, Roselle and Schere<sup>20</sup>, and the model developed by Lopez *et al.*<sup>21</sup>. The latter is specifically designed to determine the influence of light hydrocarbons (alkanes, alkenes) and terpenic hydrocarbons on the evolution of oxidants such as ozone, PAN, CO and nitric acid within the boundary layer.

An outcome of the validation experiments is to specify the nature of the principal active compounds and their spatial and temporal distribution. With these considerations in mind, we were led to design an analytical device for volatile organic compounds, which has been previously described in detail<sup>22</sup>. This device executes automatically the following sequences: (i) preconcentration on adsorbent polymer, (ii) thermal desorption, (iii) chromatographic analysis.

The apparatus is operated by a controller, programmed in such a way to function continuously in real time over long periods. Indeed, frequency of data collection cycles must be high enough to allow a precise investigation of diurnal and seasonal variation cycles of biogenic hydrocarbons, the search of their sources and the determination of their emission rates and fluxes.

The objective of the present study was to determine the daily variation cycles of the concentration of the principal atmospheric monoterpenes at various heights and to test the working order of the automated device on the experimental site.

The work is part of the European research plan EUROTRAC-BIATEX whose scientific objectives are the following<sup>23</sup>: (i) investigation of the mechanisms for uptake and production of trace constituents in relevant European ecosystems, and (ii) evaluation of regional fluxes of these trace constituents on seasonal and annual scales.

## EXPERIMENTAL

### *Sampling site*

The research station of Schachtenau is located at the catchment Große Ohe center (19 km<sup>2</sup>, 98% forested) in Bayerische Wald, National Park, in the middle of the Bavarian forest, close to the city of SPIEGELAU (Germany). The station lies at an altitude of 807 m, while the surrounding relief ranges between 770 and 1450 m. The forest includes mainly two varieties of trees, i.e. 86% of spruce *Picea abies* (L.) Karst, being between 80 and 100 years old and having an average height of 28 m, and 14 % of beech *Vaccinium*. The catchment Große Ohe skirts the Czechoslovakian border over several kilometers.

A 51 m high tower equipped with all necessary measurement apparatus allows to work at several altitude levels and to collect an important number of meteorological parameters, either permanently, as for NO<sub>x</sub>, O<sub>3</sub>, SO<sub>2</sub>, or periodically in the course of specific scientific missions, as for NH<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, terpenes, PAN, organic acids, etc.

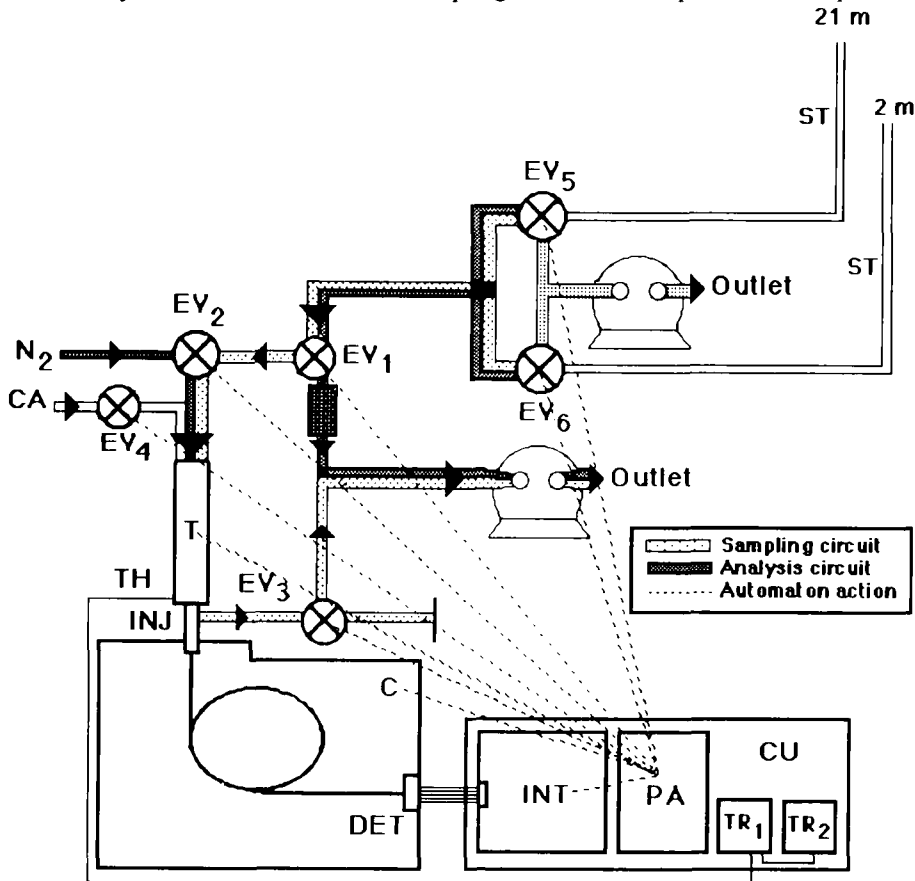
The scientific mission relevant to the present work was held from September 19th to September 27th, 1989.

### Sampling and analysis

The gas chromatograph which constitutes the main analytical device is equipped with a preconcentration/thermodesorption module. The various sequences of the analytical process are monitored by a programmable controller (Figure 1).

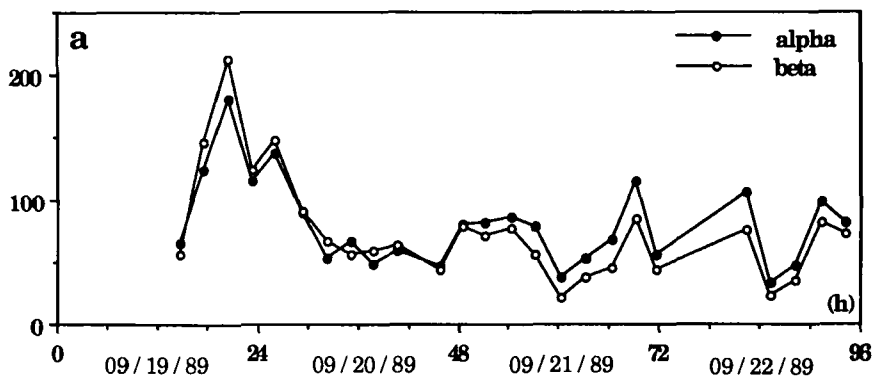
Calibration is carried out on the experimental site by spiking standard terpene solutions on the adsorbent (Tenax TA). The latter is then submitted to a thermodesorption/analysis cycle. At the end of the measurements campaign, the standardization is checked again by using permeation or diffusion generators. Both methods lead to concordant results.

The analytical device used on the sampling site differs in part from the previously

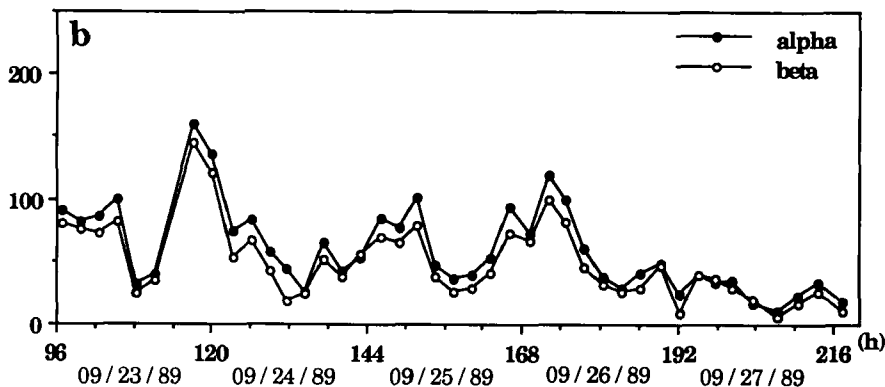


**Figure 1** Automated device for BIATEX campaign (September 1989). ST: Sampling Tube; EV<sub>1..6</sub>: Electrovalves; CA: Compressed Air; TH: Thermocouple; INJ: Injector; T: Trap; C: Chromatograph; DET: Detector; INT: Integrator; PA: Programmable Automaton; CU: Command Unit; TR<sub>1,2</sub>: Temperature Regulators.

Terpene (pptV)



Terpene (pptV)



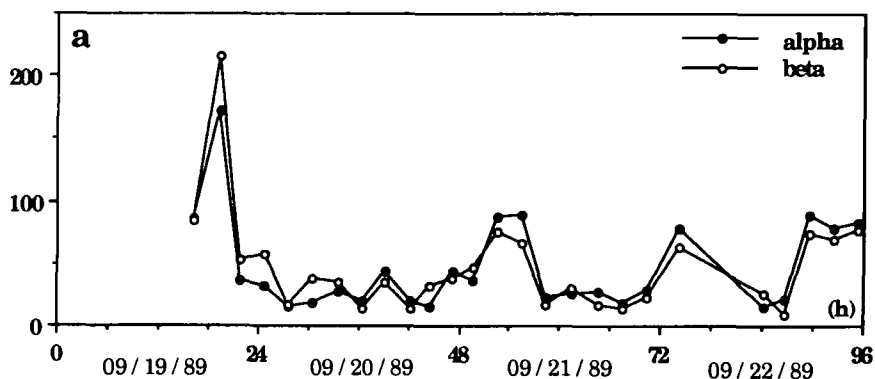
**Figure 2** Atmospheric concentrations of  $\alpha$ - and  $\beta$ -pinene at 2 m from (a) 09/19/89 to 09/22/89 and (b) 09/23/89 to 09/27/89.

described laboratory prototype<sup>22</sup>; the generator originally used to supply standard terpene samples is replaced by an atmospheric sampling module. This device allows automated and alternate sample collection at 2 m above ground level and at 21 m within the canopy. The period of a full sampling/analysis cycle is of the order of one hour. We are presently attempting to reduce it in order to increase the frequency of data collection.

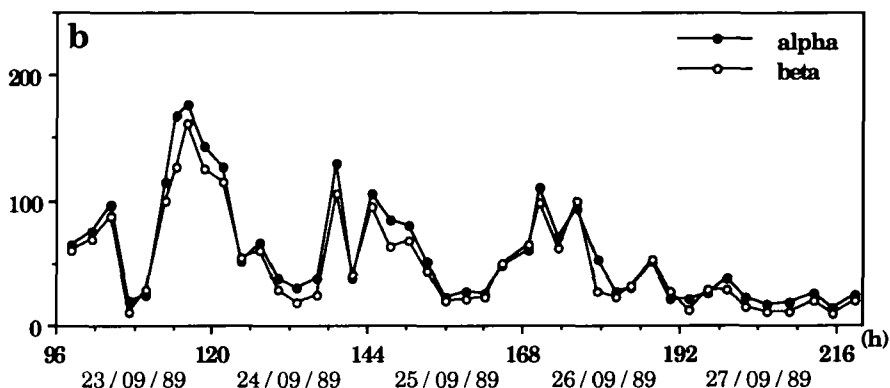
During the measurements campaign, the whole equipment was installed under a tent. We have experienced very different meteorological conditions, namely, sun, fog and heavy rainfalls. Under such conditions, the apparatus remained in good working order.

A current problem inherent in the use of a preconcentration Tenax trap is that undesirable side products like benzaldehyde, acetophenone and phenol, are accumulated within the adsorbent and are thermodesorbed<sup>24-26</sup>. The chromatographic peaks of these compounds may overlap with the isoprene peak appearing within the first 2 min under the chromatographic conditions used. We have overcome this problem by using the trap continuously, thereby preventing the accumulation of undesirable products. It is thus possible to carry out a satisfactory isoprene analysis.

## Terpene (pptV)



## Terpene (pptV)



**Figure 3** Atmospheric concentrations of  $\alpha$ - and  $\beta$ -pinene at 21 m from (a) 09/19/89 to 09/22/89 and (b) 09/23/89 to 09/27/89.

## RESULTS

The concentration profiles of  $\alpha$ -pinene and  $\beta$ -pinene recorded at 2 and 21 m, obtained from September 19th to 27th, are reported in Figures 2 and 3, respectively. These profiles show a variation of concentrations between day and night, with the highest terpene concentrations being observed at night.

During day time, terpenes appear to be practically destroyed through photochemical reactions with ozone and  $\text{OH}^\cdot$  radicals. At night, due to the absence of reaction with  $\text{OH}^\cdot$  and the decrease of reactions with ozone, there is an important accumulation of terpenes in spite of their potential reaction with  $\text{NO}_3^\cdot$  radicals. Immediately after sunrise, the terpene concentrations are seen to decrease due to the predominance of photochemical processes.

A number of research groups working in Bavaria (Kreuzig *et al.*<sup>27</sup> and Steinbrecher *et al.*<sup>28</sup>) and on other sites (Bufalini<sup>29</sup>, Ciccioli *et al.*<sup>30</sup>, Roberts *et al.*<sup>31</sup>, Riba *et al.*<sup>32</sup>, Yokouchi and Ambe<sup>33</sup>, Clement *et al.*<sup>34</sup>) have reported closely related terpene variations. By contrast,

Yatagai *et al.*<sup>35</sup>, Bufler and Wegmann<sup>36</sup> have observed an increase in the ratio of biogenic compounds during the day, with a maximum reached at the end of the afternoon and a strong decrease following sunset. According to these authors, the observed nocturnal minimum may be due to the low nocturnal temperatures that may reduce the emissions, and also to a high amount of nitrate radicals in the atmosphere. Our experiments carried out during the night of September 19–20, at 21 m, show maximum terpenic concentrations at 7 p.m.

The terpene concentrations recorded during our experiments ranged between 6 pptV (36 ng m<sup>-3</sup>) and 216 pptV (1300 ng m<sup>-3</sup>) and can be accounted for by the occurrence of relatively low temperatures, rather short sunny periods, and fog followed by rainfalls at the end of the experiment. These concentrations are of the same magnitude as those measured by other authors in the presence of the same tree species (*Picea abies*). For example, Jüttner<sup>37</sup> has reported concentrations of  $\alpha$ - and  $\beta$ -pinene of 175 pptV (974 ng m<sup>-3</sup>) and 140 pptV (776 ng m<sup>-3</sup>), respectively, in the Black Forest (Germany) in September. Bufler and Wegmann<sup>36</sup> have recorded maximum values of 96 pptV (560 ng m<sup>-3</sup>) for  $\alpha$ -pinene and 46 pptV (270 ng m<sup>-3</sup>) for  $\beta$ -pinene in the Welzheim (Germany) forest in September. These values are related to the occurrence of low temperatures during the experiment (5–11°C).

In order to provide a better interpretation of the observed variations of the concentrations of biogenic hydrocarbons and of their dependence on meteorological conditions, we have classified our results into diurnal and nocturnal periods and according to the three kinds of weather encountered, sunny and foggy and rainy. The results are reported in Table 1.

**Table 1**  $\alpha$ - and  $\beta$ -pinene concentrations (pptV) in relation with the meteorological conditions observed during the BIATEX campaign (September 1989).

	Sunny weather (09/19–23)			Foggy weather (09/24)			Rainy weather (09/25–27)		
	day	night	day and night	day	night	day and night	day	night	day and night
<i>Altitude: 2 m</i>									
$\alpha$ -Pinene									
min-max	31–123	46–180	31–180	25–101	42–136	25–136	11–100	18–119	11–119
average	64.2	99.7	80.9	58.2	78.6	70.1	39.4	53.1	45.6
	n = 17	n = 15	n = 32	n = 5	n = 7	n = 12	n = 12	n = 10	n = 22
$\beta$ -Pinene									
min-max	21–146	43–212	21–212	18–79	37–121	18–121	6–81	9–100	6–100
average	55.8	94.9	74.1	42.8	66.7	56.7	31.2	44.7	37.3
	n = 17	n = 15	n = 32	n = 5	n = 7	n = 12	n = 12	n = 10	n = 22
$\alpha/\beta$	<b>1.15</b>	<b>1.05</b>	<b>1.09</b>	<b>1.36</b>	<b>1.18</b>	<b>1.24</b>	<b>1.26</b>	<b>1.19</b>	<b>1.22</b>
<i>Altitude: 21 m</i>									
$\alpha$ -Pinene									
min-max	15–167	15–176	15–176	30–129	38–126	30–129	17–94	14–110	14–110
average	51.2	69.6	60.1	61.9	81	69.8	34	42.7	38.4
	n = 18	n = 17	n = 35	n = 7	n = 5	n = 12	n = 11	n = 11	n = 22
$\beta$ -Pinene									
min-max	9–126	13–216	9–216	18–106	40–115	18–115	10–99	9–98	9–99
average	45	70.1	57.2	49.7	73.4	59.6	27.9	40.3	34.1
	n = 18	n = 17	n = 35	n = 7	n = 5	n = 12	n = 11	n = 11	n = 22
$\alpha/\beta$	<b>1.14</b>	<b>0.99</b>	<b>1.05</b>	<b>1.24</b>	<b>1.10</b>	<b>1.17</b>	<b>1.22</b>	<b>1.06</b>	<b>1.13</b>

n = number of measurements

The following observations can be made:

Nocturnal concentrations of terpenes are higher than diurnal ones, regardless of the height at which the measurements are made and of the weather. On an average, the diurnal/nocturnal terpene concentration ratio varies from 1.25 under rainy conditions to 1.7 under sunny conditions.

The measurements carried out under rainy conditions, at daytime or nighttime, lead to terpene concentrations that are 1.5 to 2 times lower than in the absence of rain. This is probably a consequence of the washing phenomenon and of the absence of atmospheric stability. Closely related discrepancies have been observed by Rasmussen and Went<sup>38</sup>, Seila<sup>39</sup> and Riba *et al.*<sup>32</sup>.

A decrease of the concentrations measured at an altitude of 2 m is observed in foggy weather in comparison with sunny conditions, at any time of the daily cycle. The reverse tendency is observed at 21 m. A reasonable explanation for these discrepancies is the following: at low altitude, under the vegetation cover, where the influence of the sun remains low, the photochemical atmospheric reactions are not significantly affected by foggy weather. This decrease of the terpene concentrations is principally due to the low temperatures observed in the presence of fog.

At an altitude of 21 m, the fog causes a decrease of the luminosity by a factor of two compared to sunny conditions. Hence, the degradation rates of the terpenes by photochemical reactions may decrease more strongly than the emission rates, resulting in an increase of their concentrations in the atmosphere.

The two monoterpenes investigated in this work exhibit comparable concentrations during daytime and at night, with a slight predominance of  $\alpha$ -pinene.

The concentration ratio  $\alpha$ -pinene/ $\beta$ -pinene ranges between 0.99 and 1.36. Jüttner<sup>40</sup> has reported an  $\alpha/\beta$  ratio of 1.2.

A comparison of the plots (Fig. 4) showing the variations of the sum of the terpene concentrations versus time at 2 and 21 m does not clearly indicate the existence of a ground source for terpenes. The latter hypothesis could be considered during the first three days (09/20–21–22) for which higher concentrations were detected at 2 m. Similar results were reported by Riba *et al.*<sup>32</sup>, Bufler and Wegmann<sup>36</sup> and Kreuzig *et al.*<sup>41</sup>.

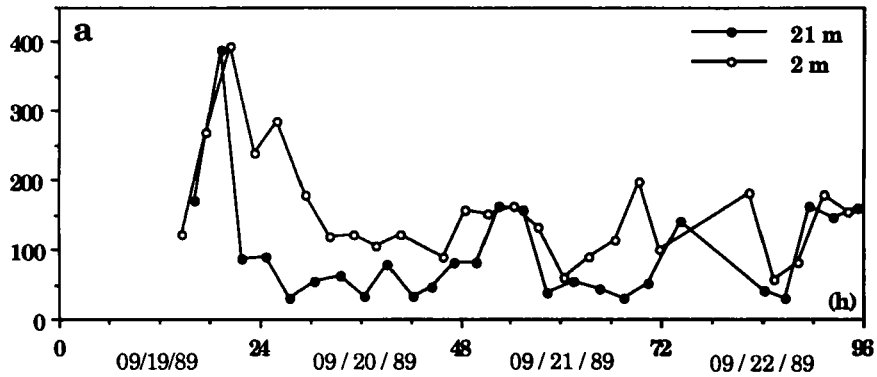
The ground level source could be either the important pine needle layer over the forest soil<sup>31,42</sup> or the presence of neighbouring trees having scarifications that may account for an exceptional emission of terpenes. During the first days (09/19–22), the existence of the nocturnal and diurnal temperature inversions may explain the high concentration gradients between 2 m and 21 m. Furthermore, the terpene losses via photochemistry are less important under the canopy (2 m), where luminosity is low, than at 21 m. Starting from the night of 09/22–23, due to an absence of temperature inversion, the atmospheric unstability as well as the washing phenomenon under rainy conditions lead to an important decrease of the concentration gradient between the two heights, which tends to disappear.

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## Terpenes (pptV)



## Terpenes (pptV)

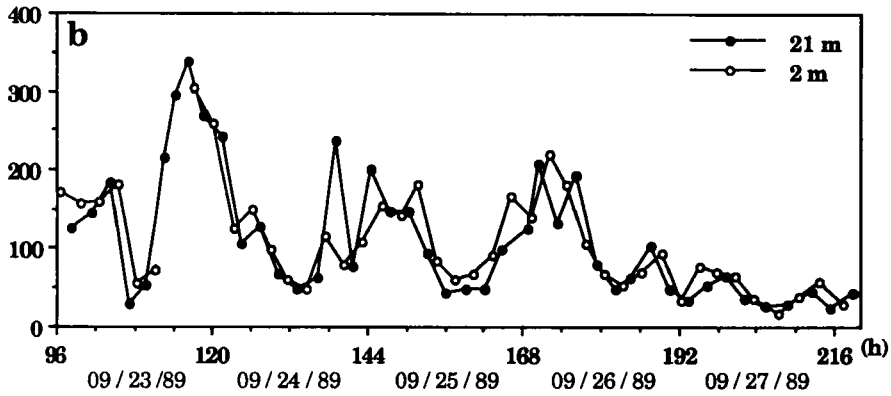


Figure 4 Total terpenic concentrations at 2 and 21 m from (a) 09/19/89 to 09/22/89 and (b) 09/23/89 to 09/27/89.

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