



## Determination of $H_2O_2$ in the Berlin city plume during BERLIOZ

A. Boddenberg, G. Dallmann, A. P. Ligon, W. V. Turner and S. Gäb, Bergische Universität-Gesamthochschule Wuppertal, FB 9 Analytische Chemie, Wuppertal, Germany  
 D. Großmann and G. Moortgat, Max Planck Institut für Chemie, Atmosphärenchemie, Mainz, Germany  
 F. Slemr, Fraunhofer Institut für Atmosphärische Umweltforschung, Garmisch-Partenkirchen, Germany  
 W. Wieprecht and D. Moeller, Brandenburgische Technische Universität, Cottbus, Germany



As part of the BERLIOZ field campaign in 1998, hydroperoxides were determined at four ground stations predicted to be downwind of Berlin during summer smog periods. At the field stations Eichstaedt and Lotharhof the hydroperoxides were determined with commercially available hydroperoxide analysers, while at Pabstthum and Menz optimised HPLC methods were used. All the results presented here are based upon the reaction of the hydroperoxides with p-hydroxyphenyl acetic acid, catalysed by horseradish peroxidase. The results from Menz were backed up by a parallel HPLC determination with a nonenzymatic post-column reaction system. The sampling by both the hydroperoxide analysers and the HPLC method in Pabstthum was by means of sampling coils. In Menz cryosampling at  $-78^\circ\text{C}$  was used. Prior to the BERLIOZ field campaign all the procedures were subjected to intercalibration; the calibration of the procedures during the campaign was carried out with liquid samples.

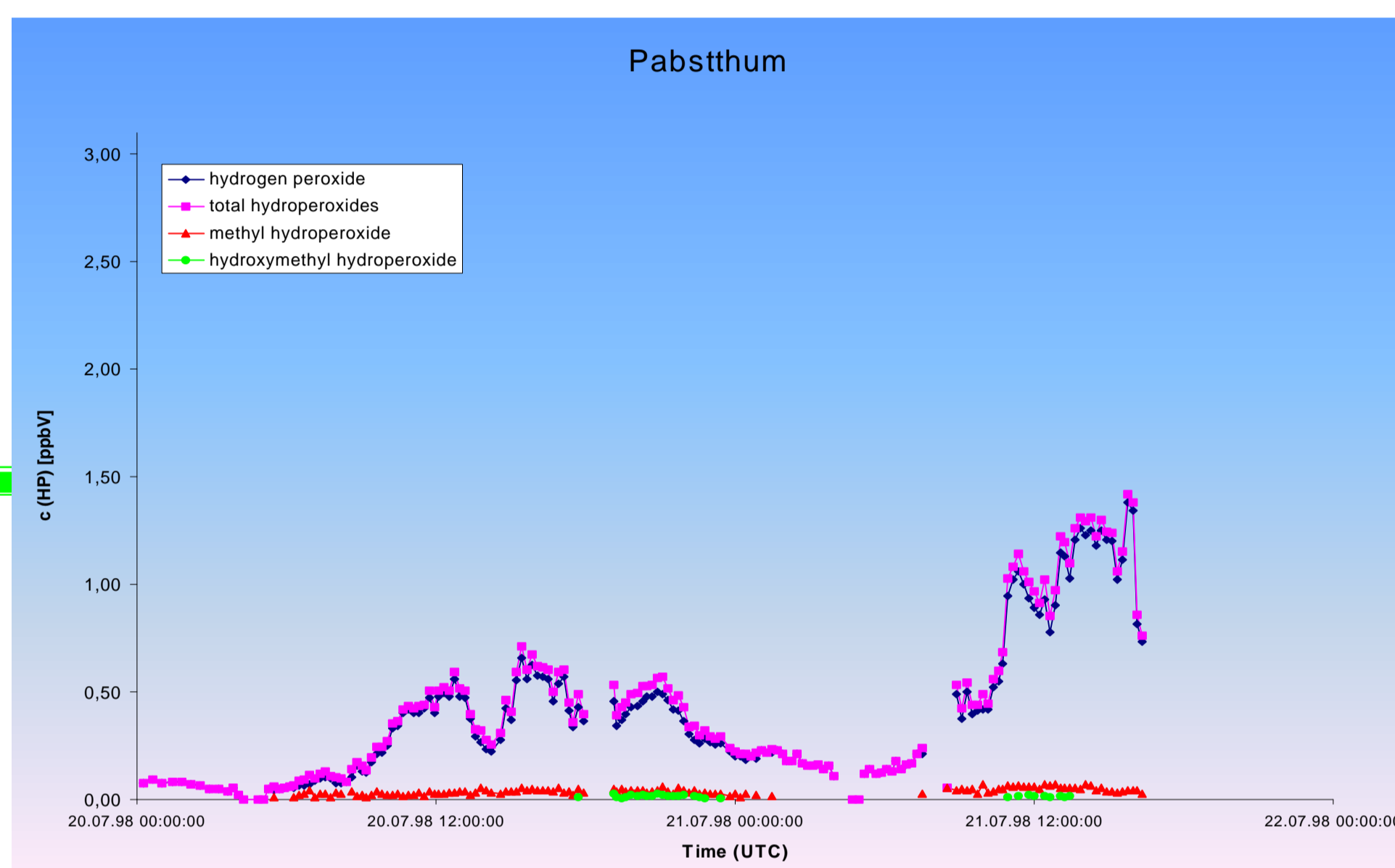


Fig. 1: Variation of the peroxide concentrations on 20th and 21st July 1998 at Pabstthum

Unlike the HPLC procedures, which identify and quantify the individual hydroperoxides after chromatographic separation, the commercial hydroperoxide analysers can only distinguish between  $H_2O_2$  and organic hydroperoxides as a class. The destruction of  $H_2O_2$  by catalase in the latter method is commonly fraught with problems. For this reason only the total hydroperoxide concentration can be reported for the field station Lotharhof and only the  $H_2O_2$  for Eichstaedt.

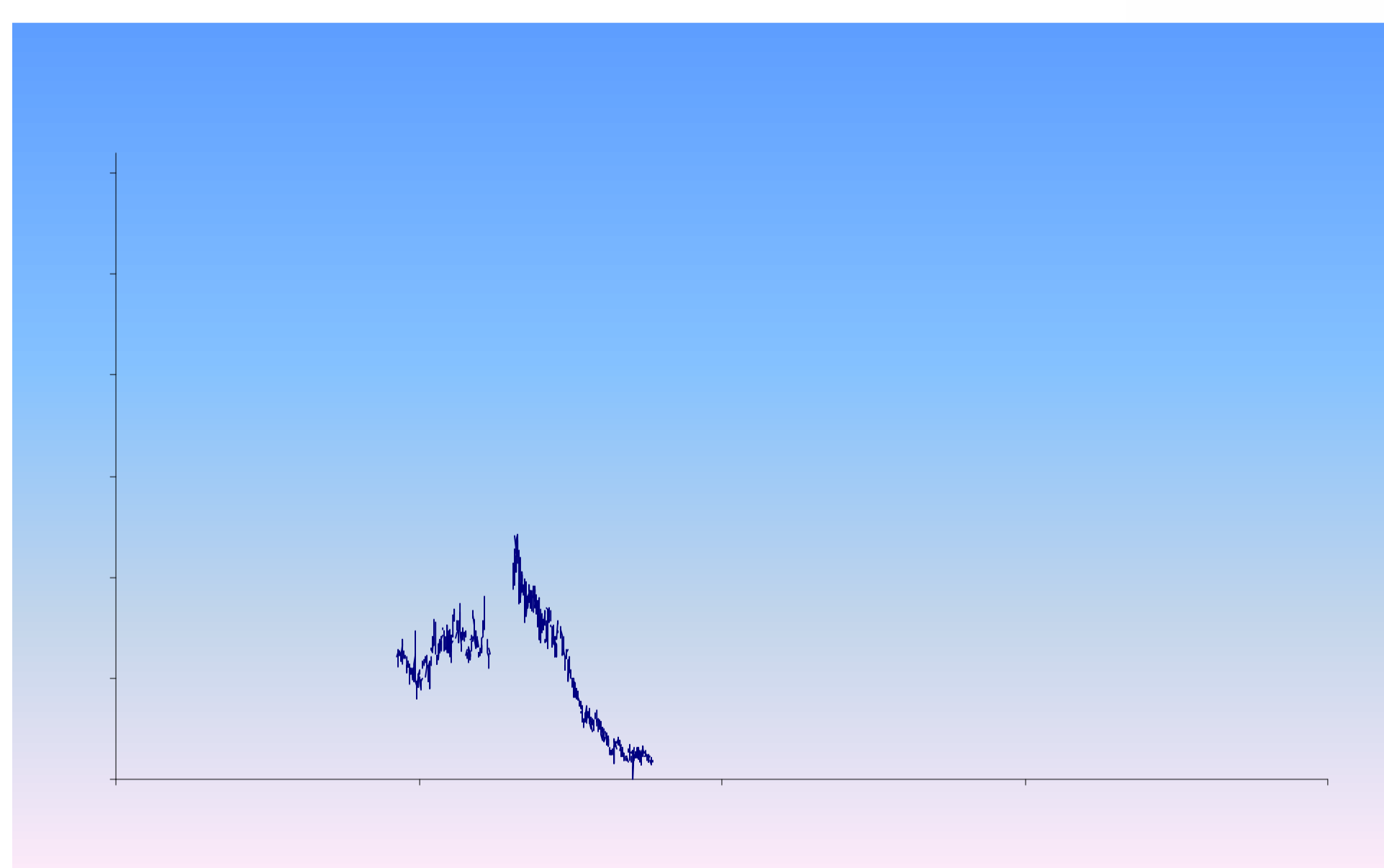


Fig. 2: Variation of the hydrogen peroxide concentration on 20th and 21st July 1998 at Eichstaedt

The total hydroperoxide concentration during the intensive part of the campaign, 20-21 July 1998, amounted to as much as 3 ppb in the afternoon of the second day. The variations in the concentrations over the course of the day at the several stations are pretty much comparable; thus the hydroperoxide concentration attained a maximum of ca. 1.5 ppbV at the field stations Eichstaedt, Lotharhof and Menz during the late afternoon of 20.07.98. In Pabstthum there was a maximum at the same time, but it was, at only 1 ppb, significantly lower than those at the other three stations mentioned.

An increase in the concentrations observed in the night at three stations was particularly pronounced at the Menz station. The questions arise as to whether this effect arose from the sampling technique and possible artefacts and why the hydroperoxide concentrations at the Menz station—perhaps caused by meteorological conditions—deviated so greatly from those at the other stations.

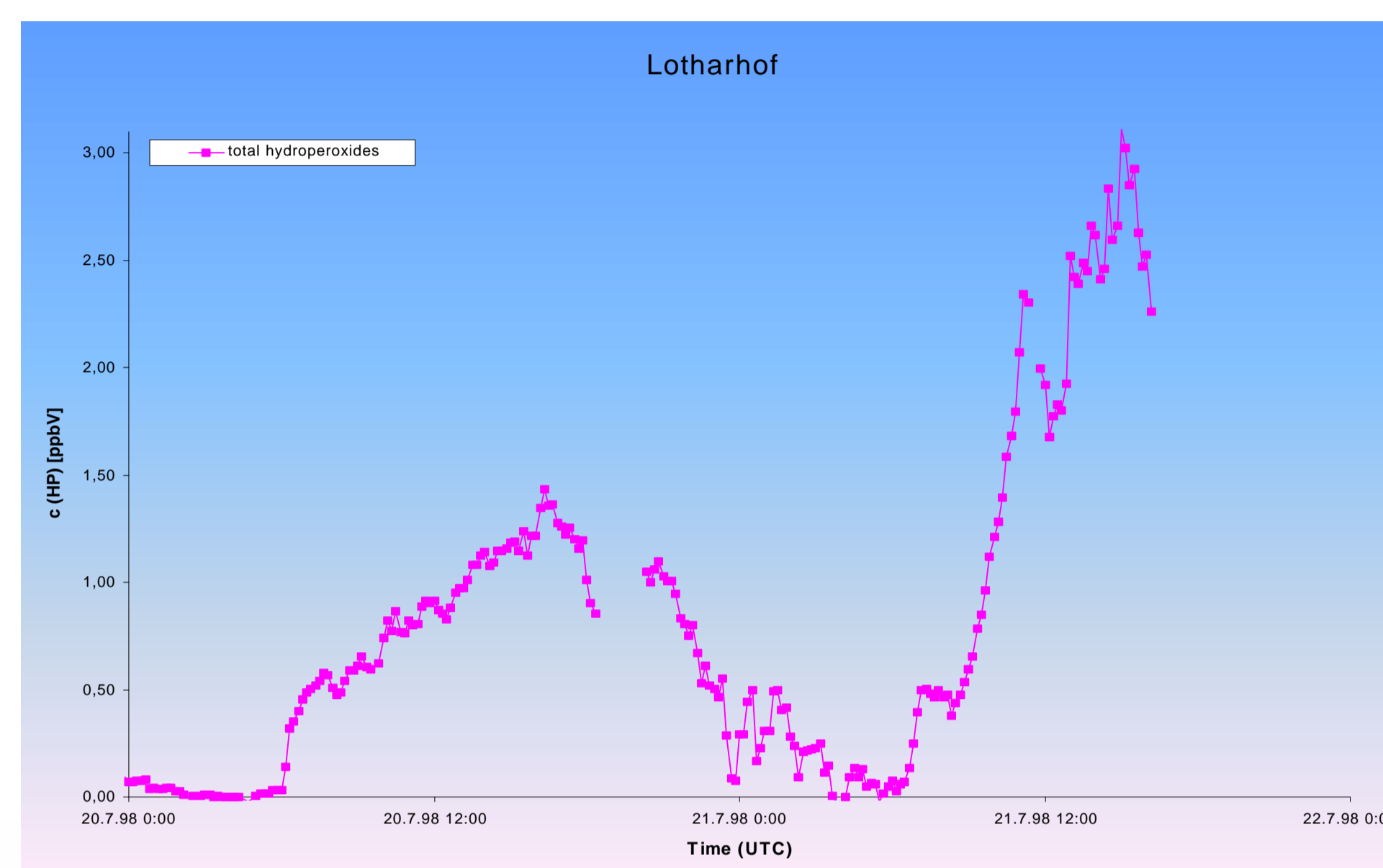


Fig. 3: Variation of the total peroxide concentration on 20th and 21st July 1998 at Lotharhof, near Braunsberg

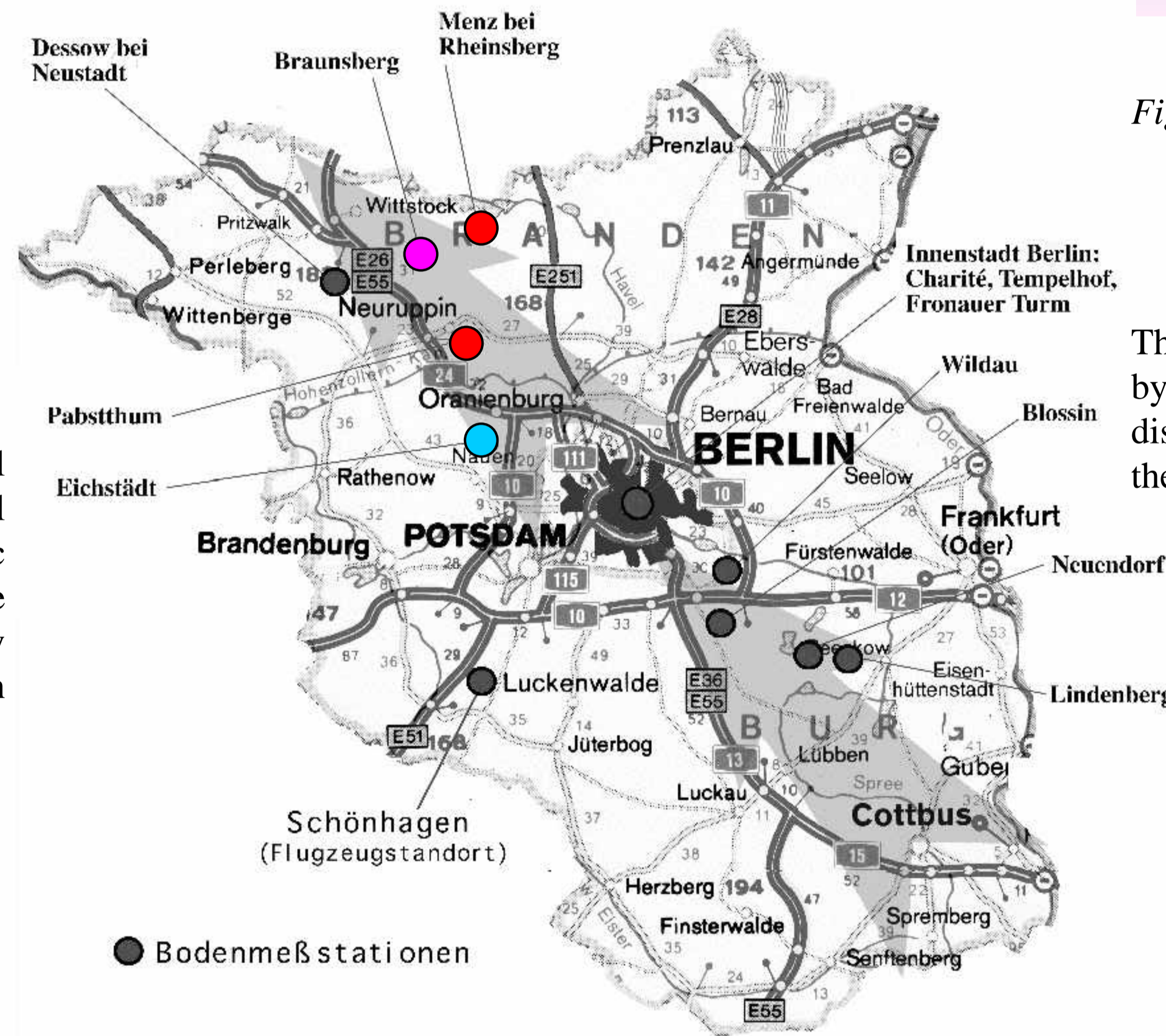


Fig. 4: BERLIOZ area and stations around Berlin

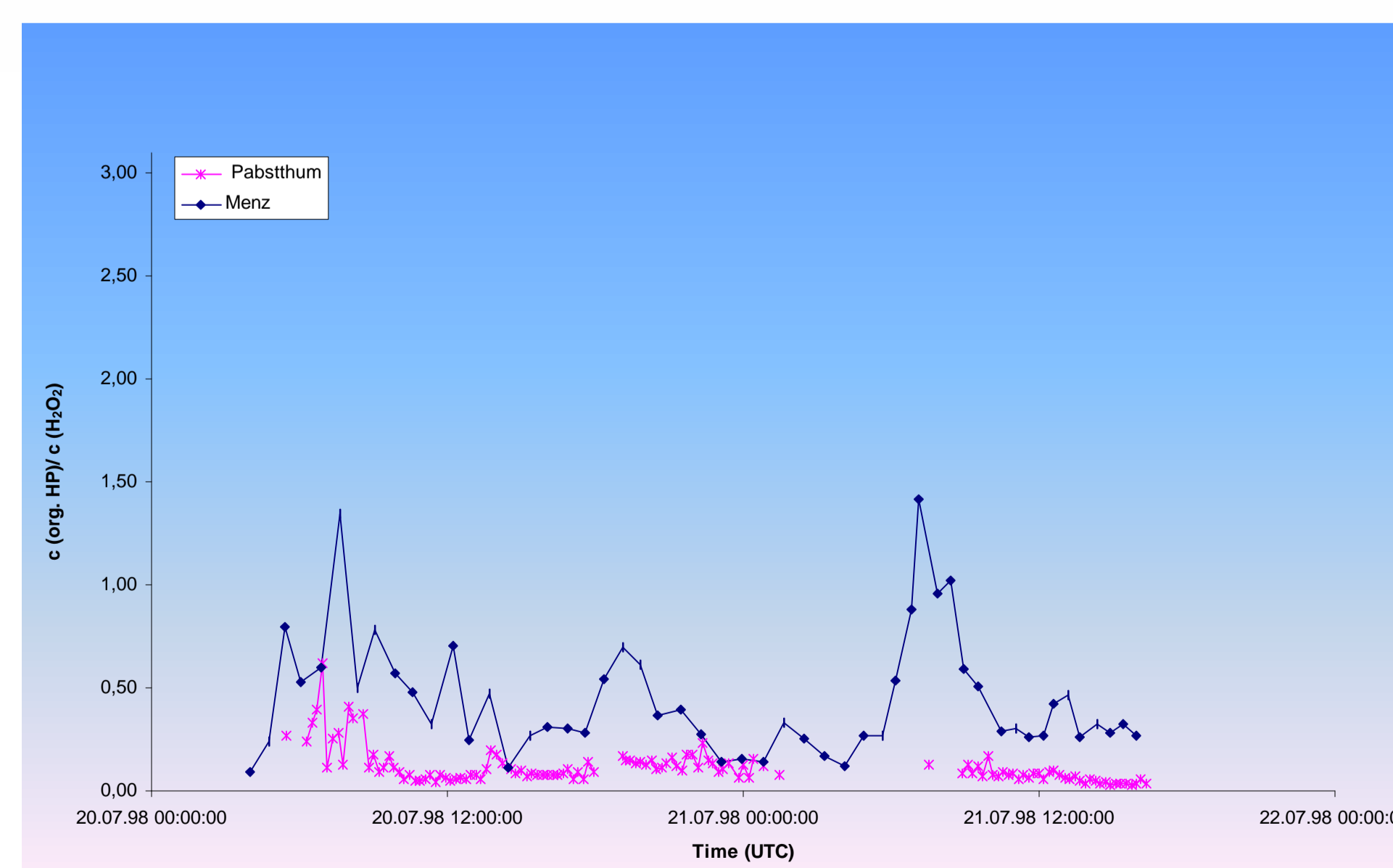


Fig. 5:  $H_2O_2$  / organic peroxide ratio on 20th and 21st July 1998 at Pabstthum and Menz

The same questions can be asked about the concentration of organic hydroperoxides: thus during the campaign period ca. five times as much organic peroxide was found at the Menz station as at Pabstthum. At neither of these two stations, however, did the total hydroperoxide concentration attain the very high levels seen at Lotharhof. Any answer to these questions has to take into consideration the fact that the great increase in the hydroperoxide concentrations was also observed with the HPLC system with a sampling coil and the fact that during the preparatory intercalibration no statistical differences were observed between cryosampling and sampling with a sampling coil, even with real samples.

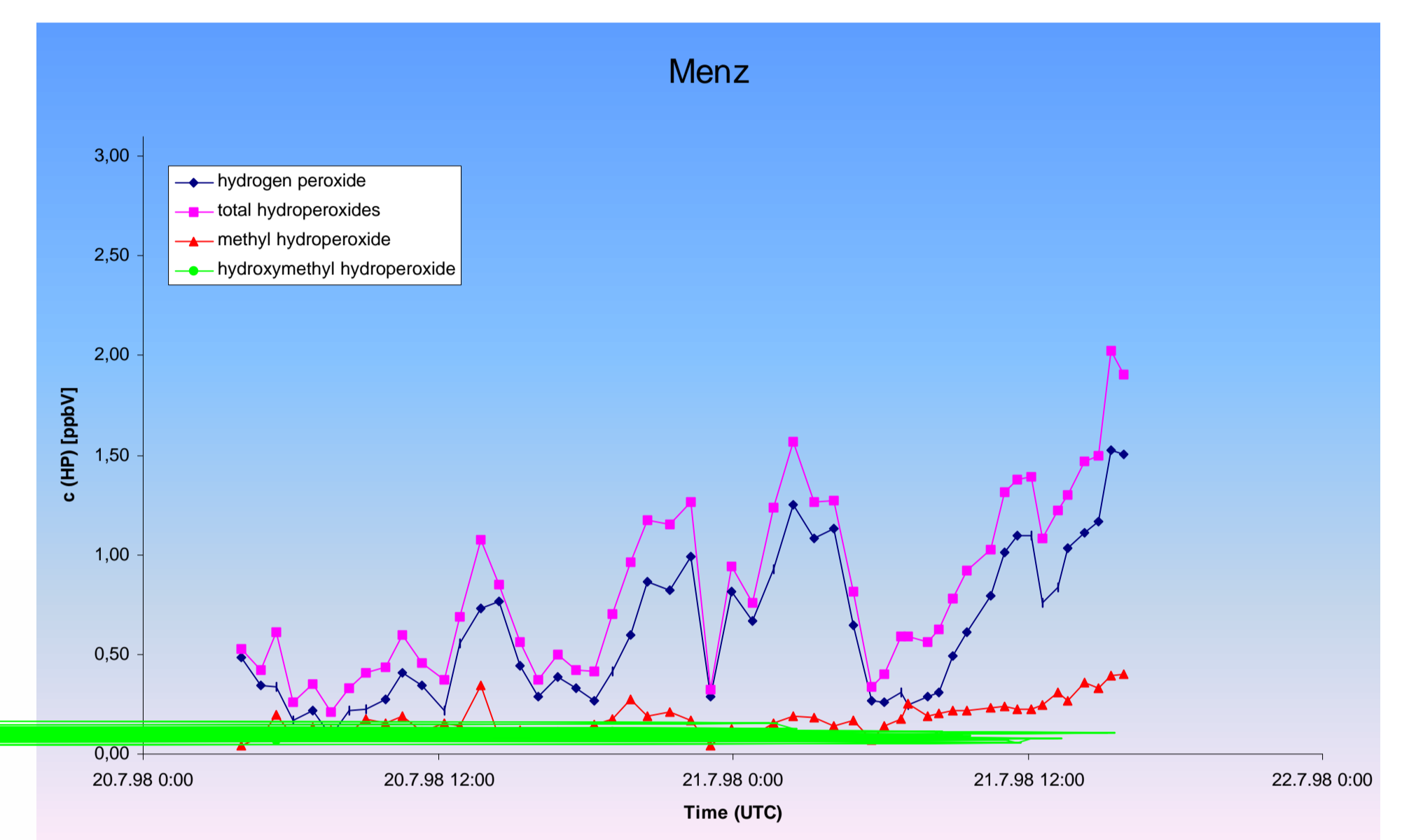


Fig. 6: Variation of the peroxide concentrations on 20th and 21st July 1998 at Menz

The revised modelling of the Berlin city plume of 20.07.98, as shown by Becker and Schaller, reveals that the air masses at the field stations discussed here had greatly different origins, so that the results from these stations cannot be expected to be directly comparable.

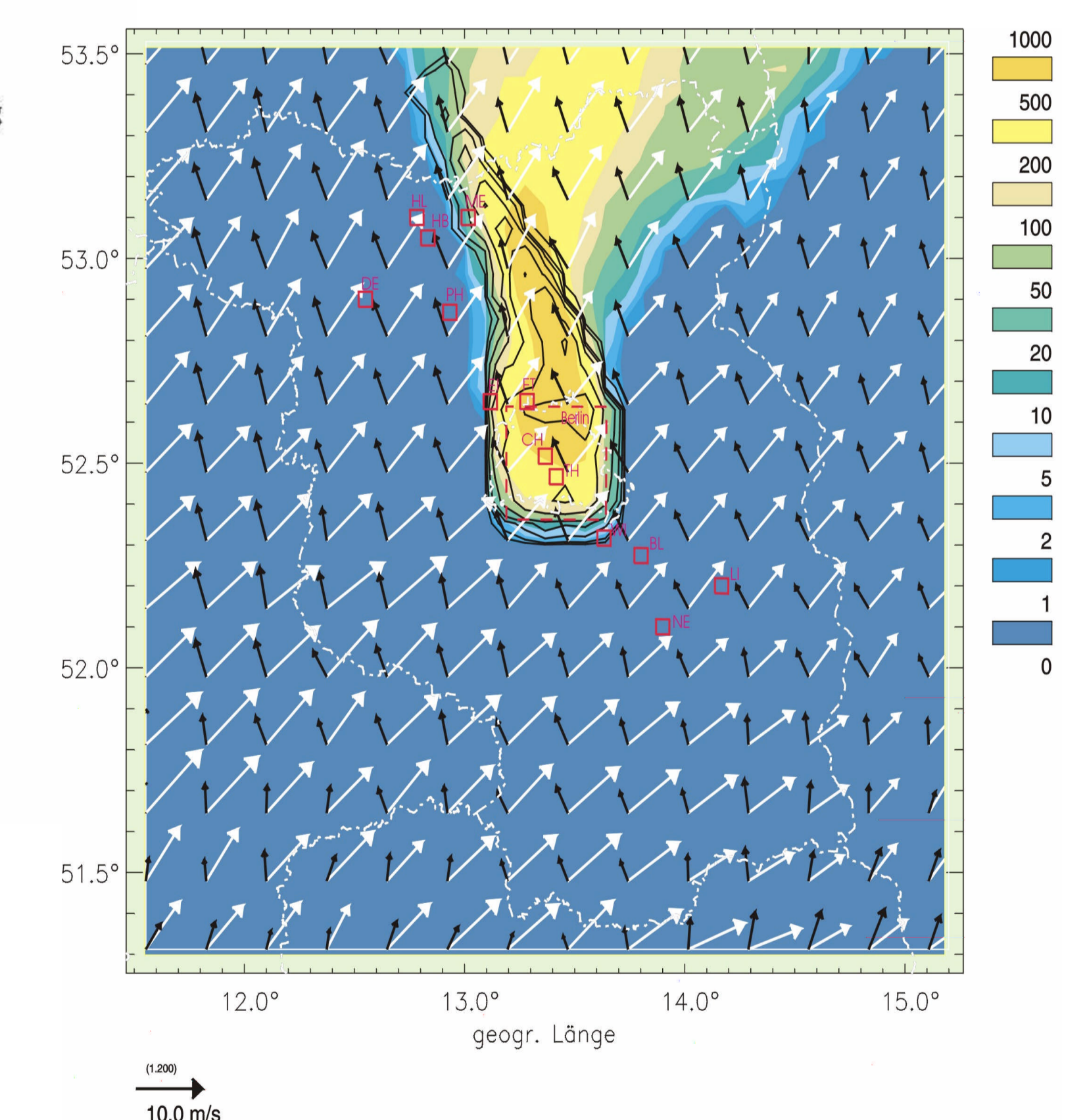


Fig. 7: Simulation of the "Berlin plume" resulting from a continuous volume emission out of the "Berlin-Box" (Figure 4) from 6 to 18 UTC. Beside the column integrated concentration (logarithmic contour interval) the concentration in the lowest 50 m, illustrating the effect of the vertical shear of the horizontal wind (see also black [ $z=35\text{ m}$ ] and white [ $z=1\text{ km}$ ] arrows) is additionally shown by the solid lines (same logarithmic scale, see left boundary). (Diagram used with permission of Prof. Schaller and Dr. Becker, University of Cottbus).