Summary

A critical investigation of literature reported precipitation-pH measurements leads to the conclusion that since the late 30th the precipitation-pH has not changed very much in Central Europe, in spite of the fact, that the SO$_2$ emission has doubled in the meantime. This finding is confirmed by some observations of the precipitation-pH in Hamburg, which is measured since 1976 with an automatic precipitation monitor, operating continuously during falling precipitation. The pH shows no pronounced yearly cycle and no dependence of the wind direction, even in those cases where a trajectory analysis proves direct transport of the air mass over the North Sea without land contact. It is concluded, that acid formation during the precipitation process is limited due to physical and chemical reasons and that on the average, the removal capacity of the precipitation for acidifying gases is exhausted, when an average pH-value slightly above 4 is reached. As a consequence of increasing SO$_2$ emission a spreading out of the area with acid rain rather than a local decrease of the pH is predicted.

1. INTRODUCTION

In 1872 R. Smith published a book entitled "Air and Rain - The beginning of a chemical climatology". In the introduction of the chapter "Rain" he wrote:

"It becomes clear from the experiments that rain-water in town districts, even a few miles distant from a town, is not a pure water for drinking; and that, if it could be got direct from the clouds in large quantities, we must still resort to collecting it on the ground in order to get it pure. The impurities of rain are completely removed by filtration through the soil; when that is done, there is no more nauseous taste of oil or of soot, and it becomes perfectly transparent. The presence of free sulfuric acid in the air sufficiently explains the fading of colours in prints and dyed goods, the rusting of metals and the rotting of blinds".
and a few sentences later:

"I do not mean to say that all rain is acid; it is often found with so much ammonia in it as to overcome the acidity; but in general, I think, the acid prevails in the town".

Smith conducted a lot of experiments to study its trace substance content. He carried out his experiments very carefully and being a person of sound diffidence, he collected the rainwater in a platinum basin which he, to prevent all mistakes, kept red-hot for sometime prior to use. If we do interpret his figures for the amount of free acid in our present understanding pH-values of 4 in the London rain, for example, were quite common. It seems to be a fruitful task, to reexamine his methods and results.

Any pH-values of precipitation, reported in the literature, must be investigated very critically with respect to collection method, analytical method and averaging procedure. For example, we find data of open gauges emptied only once every four weeks and thus representing the total, wet and dry deposition. Or in order to obtain a mean pH-value, the individual pH-values were averaged arithmetically although this should not be done with logarithms. Many authors try to avoid this difficulty by presenting frequency distributions of pH-values but their information content is also limited because the most frequent pH-value must not be coupled with the rain events producing the highest rain amounts. The best way of averaging pH-values is to calculate the average depositions (i.e. $H^+$ concentration times precipitation amount) and convert it back to the average pH. This procedure represents the pH-value measured in a very large reservoir, in which many precipitation events of several years are collected.

$SO_2$ and $NO_2$, the main acidifying gases are produced by many various sources. In Central Europe, although there are areas with major sources, the concentration differences from the different sources have leveled out to certain degree, before the gases are absorbed in clouds to form acid precipitation. Also precipitation is connected with wind from different directions, which again causes a transport from different sources and mixing equilibration of pH differences.

2. DATA

Fig 1 puts together the data available from the literature. The earliest measurements were made by Ernst in 1937/38 and Reinerz and Oberschreiberhau both some 150 km NE of Prague. The measurements were performed very careful. The average values as indicated are calculated as precipitation amount weighted averages. The data of Ernst (1938) were also published by Drischel (1940) but together wit the precipitation amount. The average pH of the events of a one-and-half year period was 4.17.

The next measurements were carried out by Harrassowitz (1956) who was looking for an impact of nuclear test explosions on the precipitation pH. From a short notice we can con-