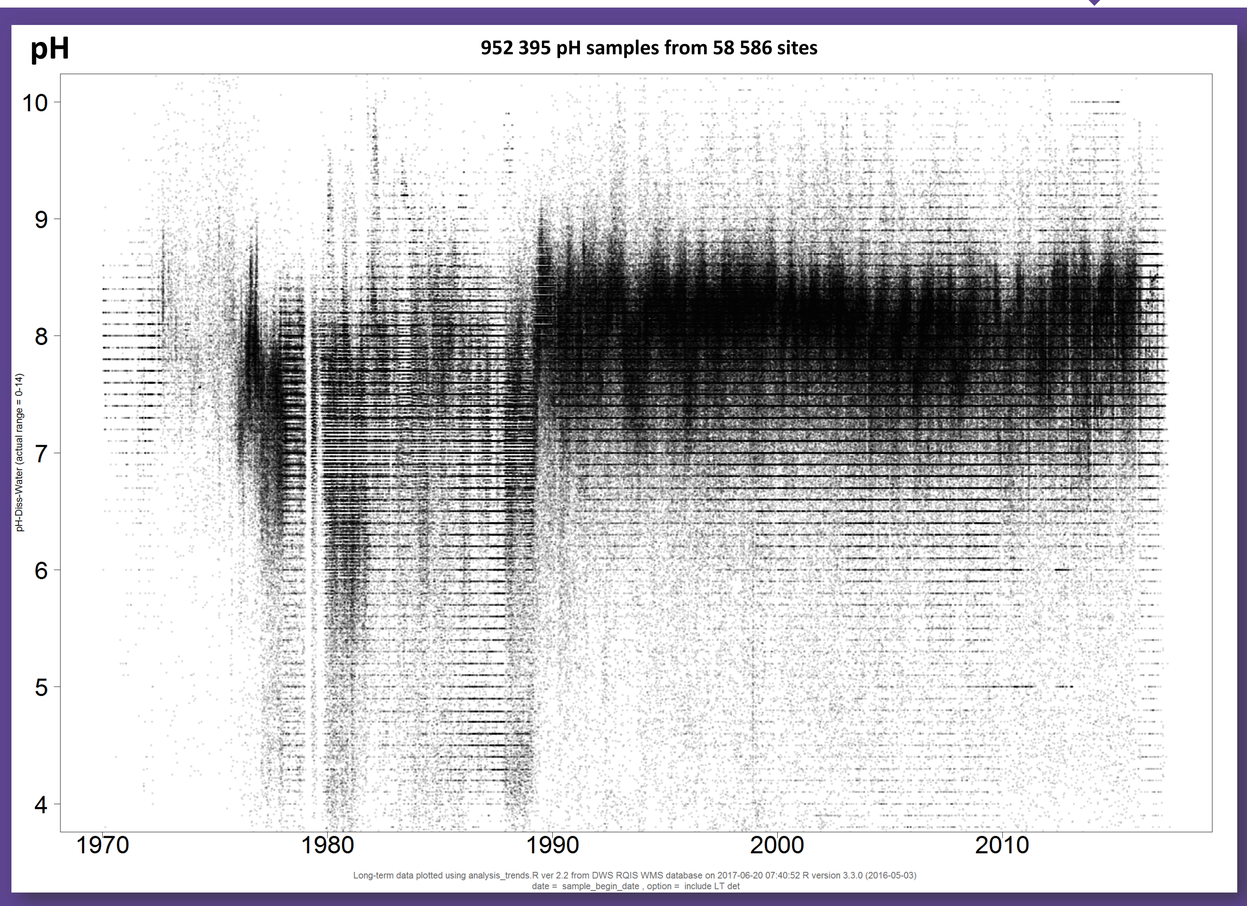
An anomaly in pH values in the South African national water quality monitoring database

South Africa's extensive National Monitoring Programmes are co-ordinated and managed by the Resource Quality Information Services directorate of the Department of Water and Sanitation (RQIS, DWS). The results are stored on the Water Management System database (WMS).

The WMS database includes long-term records of several physical and chemical water quality variables, including pH. Users of the pH data have found that it contains abnormal results during the 1980s, with a series of lower than expected values from 1978 to 1989. The drop in pH is more noticeable in acidic waters with less buffering capacity.



The pH problem

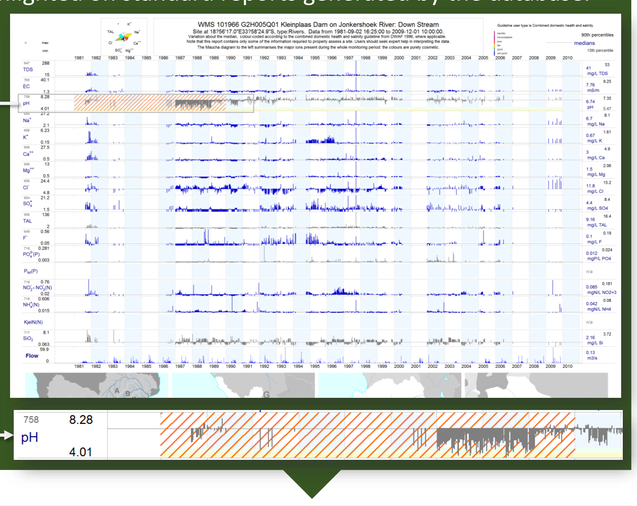
This image shows all the pH data on the South African national water quality database (WMS), from 1970 to 2016. Each point is slightly transparent, so the darker areas show where many points overlap. The horizontal striations show where manual readings were rounded to one decimal: manual – automated

Note how the bulk of the 952 395 results centre around 8 pH units, except for the period from about 1978 to 1989. During this period, the results are more widely scattered and have lower pH values.

We selected 221 sites from the national database that had at least one result per year for the period 1970-2016, and grouped them by their total alkalinity (TAL) with ranges of <10, 10-30, 30-150 and >150 mg/L TAL as $CaCO_3$.

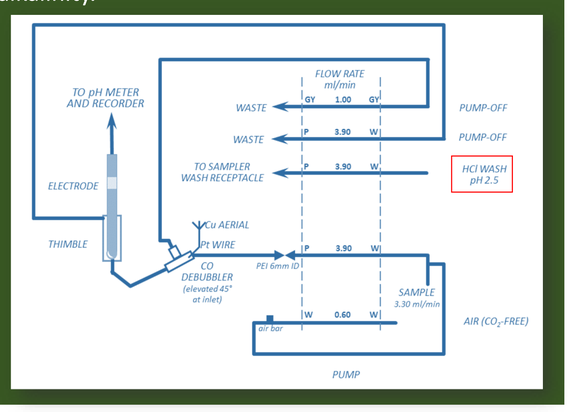
The median pH values for the highest alkalinity group were about 0.5 pH units lower during the 1978-1989 period, whereas the samples with the lowest alkalinity fell by more than 1.0 pH unit.

Whatever the reason for the anomaly, users of the WMS database should be aware of the uncertainty in pH results that were recorded before 1990. Questionable pH results are now highlighted on standard reports generated by the database.



What went wrong?

While the cause of the pH anomaly is uncertain, the bubble-segmented continuous flow method used before 1990 had a different rinse procedure from the current method (Verhoef & Engelbrecht, 1977; RQIS, 2015). Residual acid from the rinse phase might have caused a pH change. Samples with low alkalinity, and therefore weakly buffered, would be susceptible to a greater change in pH values than samples with a high alkalinity.



What can we learn from this?

We need to be cautious when analysing long-term data sets spanning several generations.

Metadata, or information about the way the results were produced, provides an essential reference for those wanting to determine long-term trends.

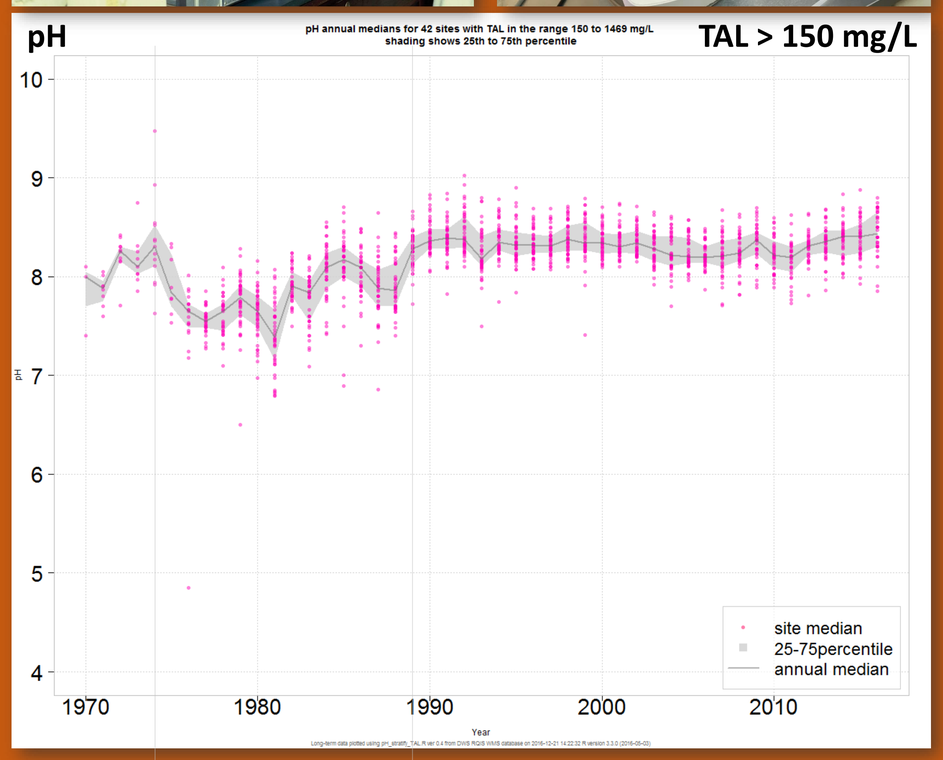
Data should be open-source, so that people can download and examine the results in different ways, and point out discrepancies that may otherwise go unnoticed.

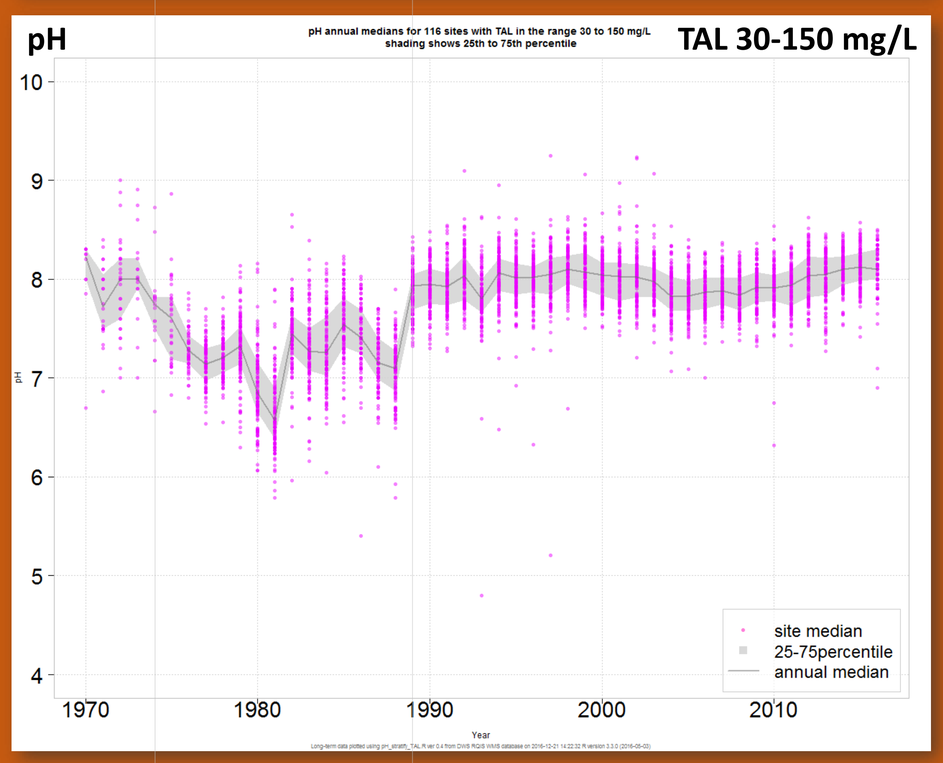
Written records of methods are a valuable resource for future researchers.

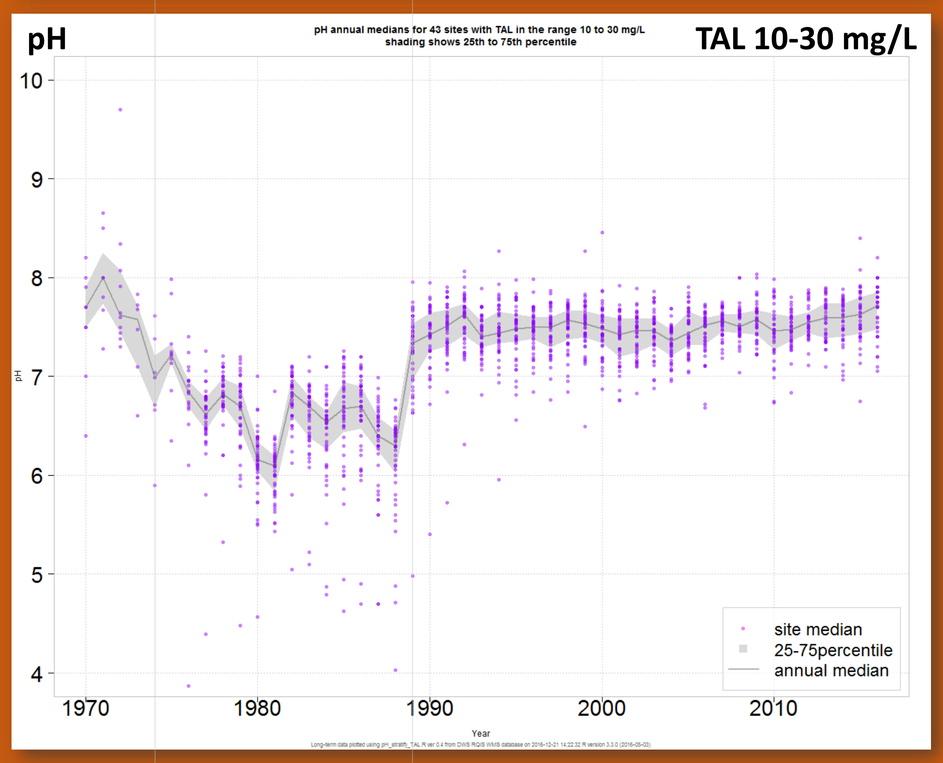
What now?

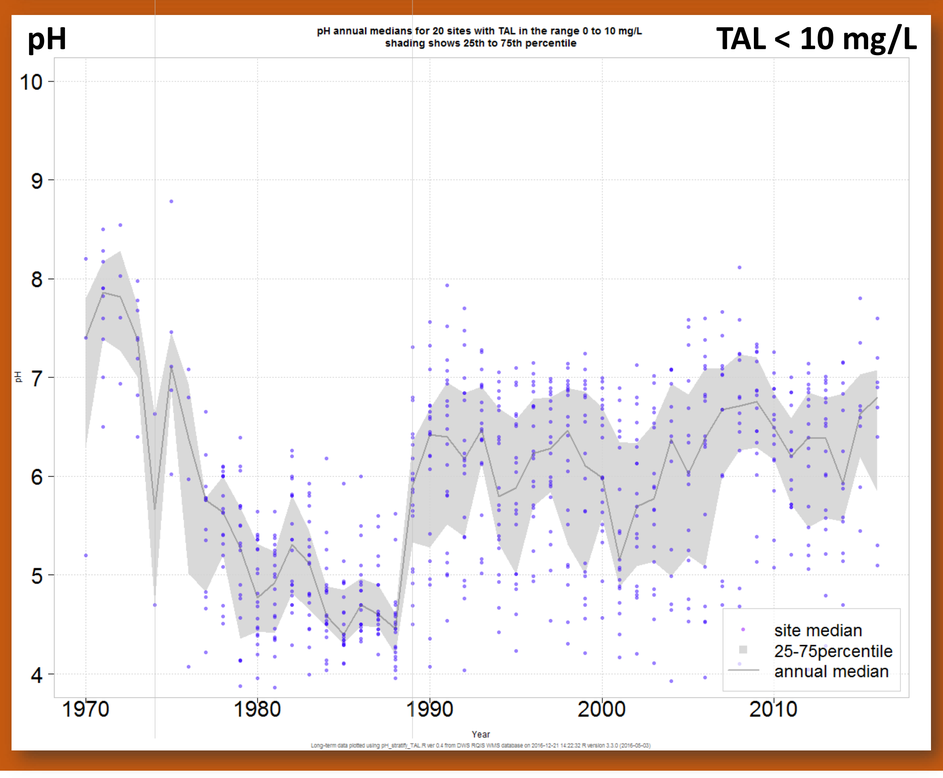
Maybe one could reconstruct the data for the period 1978-1989 by doing a statistical analysis of the pH characteristics at sites with data from 1990 onwards, and applying a correction?

In future, we need to ensure that we continue to record details about analytical methods along with the data. Publishing routine information about sampling and analysis methods may seem dull, but it can provide useful clues to scientists wanting to analyse the data many years hence.









Acknowledgements

Sebastian Jooste of RQIS tested the feasibility of using statistical analysis to retrieve the actual pH values for the anomalous period. Bets Davies provided anecdotal information drawn from her 41 years' experience with the laboratories and database. Judy Reddy advised on presenting the information.

We thank the generations of DWS auxiliary staff, technicians and scientists who have meticulously collected samples, performed analyses and recorded the data for many thousands of samples during the past 50 years.

References

Verhoef, L. H. and Engelbrecht, S. A. (1977) The automated simultaneous measurement of electrical conductivity and pH of surface and ground water samples in a routine water analysis laboratory. *Water SA* 3 (2): 72-82.

RQIS (2015). Automated determination of pH. Method 5003.2 revision 5, Resource Quality Information Services, Department of Water and Sanitation, Pretoria, South Africa.

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