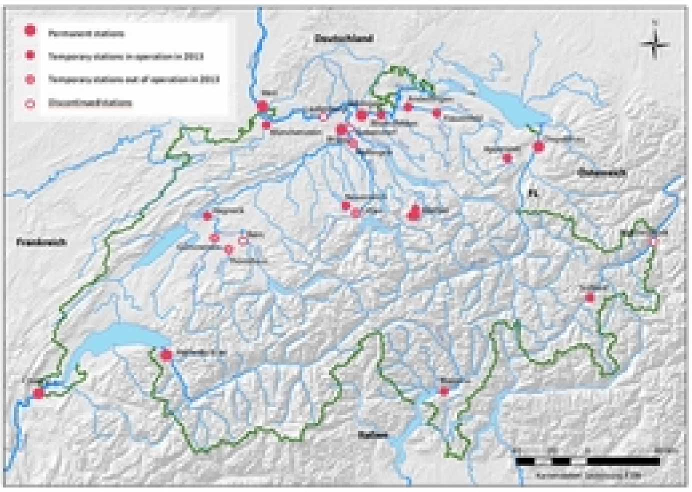
Long-term measurements in rivers demonstrate even the smallest changes

August 30, 2018 | Irene Bättig
Topics: Wastewater | Drinking Water | Pollutants | Ecosystems

A long-term study of Switzerland's major watercourses has been continuing for almost 45 years. An evaluation of the time series shows that as the climate is changing, so are geochemical processes. Most of the measuring stations show an increase in the concentrations of bicarbonate. The changes are caused by increases in temperatures, the presence of nutrients in the lakes and the acidity of the soil. On the other hand, following a peak in the late 1980s, nitrogen concentrations have been decreasing. The reasons for this are a reduced input of nitrogen in agriculture and improved elimination in wastewater treatment.

The chemical conditions in Swiss rivers have been studied since 1974 as part of the National River Monitoring and Survey Programme (NADUF). "The measuring system initiated by Eawag and the hydrology department of the Federal Office for the Environment was a completely new thing at the time", recalls Jürg Zobrist, former Eawag researcher. The measuring installation takes water samples continually as soon as a certain amount of water has flowed by and adds them to a 2-week aggregate sample. "This allows not only a measurement of concentrations in the flow samples, but also the loads can easily be calculated", explains Zobrist, who was involved when the programme was set up. At that time chemical analysis was still a long way from the possibilities offered by today's automation and levels of sensitivity. These days in Eawag's analysis laboratory, about 20 materials are identified in the water samples – among them calcium, magnesium and bicarbonate as well as various nutrients such as nitrates or total nitrogen. In addition, the flow rate, water temperature, oxygen, electrical conductivity and pH of the water are measured on an ongoing basis.

Jürg Zobrist is now retired, and Ursula Schönenberger and Stephan Hug continue the evaluation of NADUF data at Eawag. Jürg Zobrist is still an active researcher, however. In recent years he has studied the immense amount of data more closely and evaluated the measurements of geochemical parameters and nitrogen from seven stations in the NADUF measuring network. “The goal was to demonstrate and explain long-term changes from 1974 to 2013”, says Zobrist.



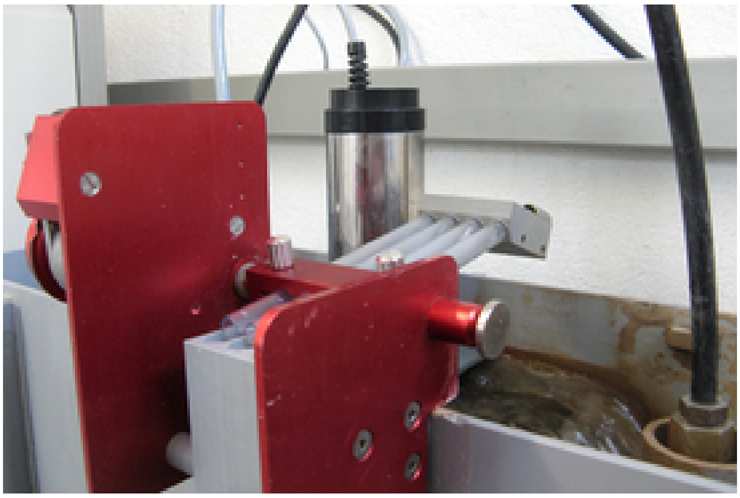
Map of NADUF stations in 2017

Water protection measures showing signs of effectiveness

His analyses demonstrate that the quantity of flowing water has scarcely changed, while the temperature has increased by 0.8 to 1.3°C. This increase has not, however, taken place in a gradual, linear fashion, but shot up in the second half of the 1980s – in the Rhone below Geneva the thermometer readings rose by 1.1°C, and in the Thur by 0.4°C. “Similar jumps in temperature were noted Europe-wide in bodies of water, ground water and in the soil”, adds Zobrist.

The concentrations and quantities of nitrogen increased markedly from 1982/83 to 1987/88. This is a somewhat delayed reflection of the great intensification of agriculture that caused the highest nitrogen excess at the beginning of the 1980s. That means that more manure and artificial fertilizers were applied than were taken up by the harvested plants. The nitrogen stored in the ground increased markedly and a corresponding quantity of nitrogen was washed into bodies of water. In addition, the unusual temperature increase in ground and water in the late 1980s led to an increase in biological mobilisation of the nitrogen.

Since the 1990s the total nitrogen load has decreased significantly – by up to 50%. “The change in agricultural fertilisation practices and improved wastewater treatment, especially the introduction of denitrification in several large wastewater-treatment plants, have made an impact,” comments Zobrist.



Sampling equipment that was revolutionary in 1974: River water is fed in at the rate of 20 to 50 L per minute by an underwater pump in the station. As soon as a quantity of water specific to the station has flowed past, the four 1 ml measuring receptacles are submerged in the constantly flowing water and then turned to empty into the hoses leading to the sample bottles in the refrigerator. An aggregate sample consisting of 800 to 4000 partial samples is thus collected. (Photo: Eawag, Jürg Zobrist)

Geochemical processes also changing

Minor but nonetheless measurable changes were also expected in the case of geochemical parameters, as the presence of calcium, magnesium and bicarbonate occurs through the weathering of calcite and dolomite stone in river watersheds. In this process, CO2 is bonded and the bicarbonate (HCO3-) thus formed enters the bodies of water. Some CO2 outgases into the atmosphere or crystallises again into calcite. These basic processes in the geochemical carbon cycle take place in equilibrium, and are dependent on environmental conditions.

Bicarbonate concentrations have increased. One reason for this, Zobrist finds, is climate change: “The air temperature increase of c. 1.5°C makes microorganisms in the ground more active, and so they breathe more and give off more CO2”. In wet ground, CO2 is dissolved as carbonic acid. A higher concentration of carbonic acid means that more stone, above all carbonate-containing minerals, is subjected to weathering and the bicarbonate concentrations increase. This process can be quantified with the help of a classic CaCO3-CO2 equilibrium scheme. Downstream of lakes, the effect of reoligotrophication is seen: because the availability of the nutrient phosphorous sank in the period under investigation, less algae grew in the lakes, so less CO2 was used up in photosynthesis. When more CO2 remains dissolved in the water, less calcite is formed.

Opposing effects overlap

In the Thur near Andelfingen the bicarbonate concentration has shown an opposite trend over the last three decades. For one thing, there is no lake upstream of this river, and so the effect of reoligotrophication is not found here. On the other hand, there are developments that have led to a decrease in weathering, according to Zobrist: “The use of agricultural fertiliser that creates acid in the soil has decreased. Deposits of acid from the atmosphere also decreased – for example through the reduction of sulphur in heating oil and above all the decrease in SO2 emissions in the former Eastern Bloc countries." These resulted in a decline in calcite weathering.

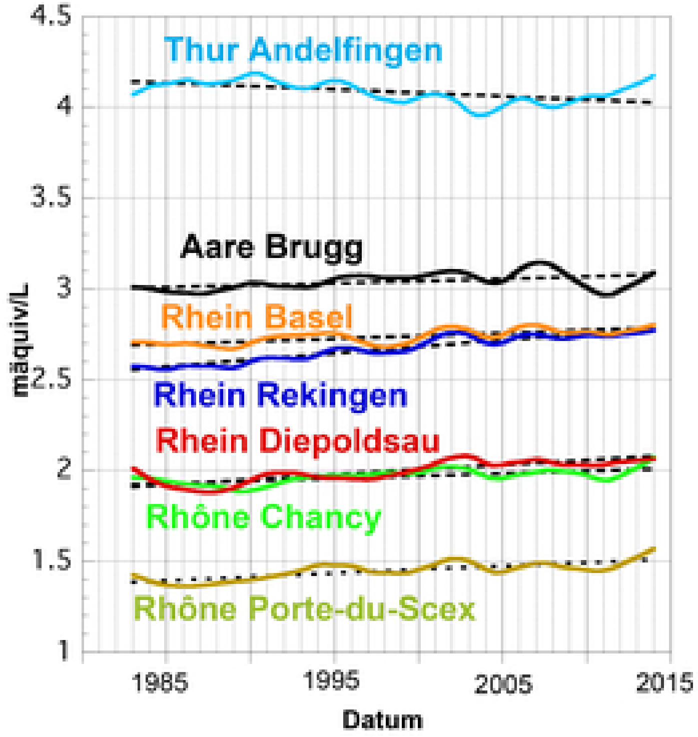
Long-term trends show that the geochemical carbon cycle is subject to changes and reacts to human influences. "The changes are minimal, but nevertheless statistically significant," sums up Zobrist, who has now retired from research, having seen through this project.

Publication

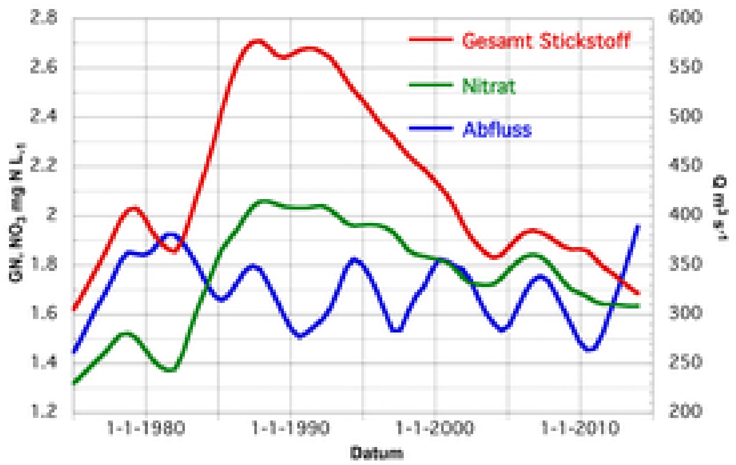
Zobrist, J.; Schoenenberger, U.; Figura, S.; Hug, S. J. (2018) Long-term trends in Swiss rivers sampled continuously over 39 years reflect changes in geochemical processes and pollution, *Environmental Science and Pollution Research*, 25, 16788-16809, doi: 10.1007/s11356-018-1679-x, Institutional Repository

More photos

Sampling station on the Glatt at Rheinsfelden (Photo: FOEN)



Changes in bicarbonate concentrations from 1983 to 2013 at seven measuring stations. The development of the measurement series averaged over 5 years is shown in colour; the dashed lines show the long-term trend, calculated by means of linear regression.



Development of the concentrations of total nitrogen (red), nitrate (green) and the flow rate (blue) in the Aare, by Brugg.

The NADUF Measuring Programme

The National River Monitoring and Survey Programme (NADUF), with its 10 permanent and, at present, 15 temporary measuring stations has been operated by the Federal Office for the Environment (FOEN), Eawag and the Swiss Federal Institute for Forest, Snow and Landscape Research WSL since 1974.

Online measurements include outflow, water temperature, pH, oxygen, and electrical conductivity. The data can be seen at the Federal Office for the Environment under Hydrological data and forecasts, dangers and warnings or current data NADUF.

In the analytical and teaching laboratory (AuA laboratory) at Eawag, the following materials and parameters are measured in the weekly water samples: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, alkalinity (bicarbonate), SO_4^{2}-, Cl-, total hardness, DOC, TOC, suspended solids and the nutrients H_4SiO_4, NO_3-, total nitrogen, DRP (o-PO_4), total phosphorous. The corresponding data files can be downloaded at the NADUF Website.

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