

Determination of trichloroacetic acid in rain water

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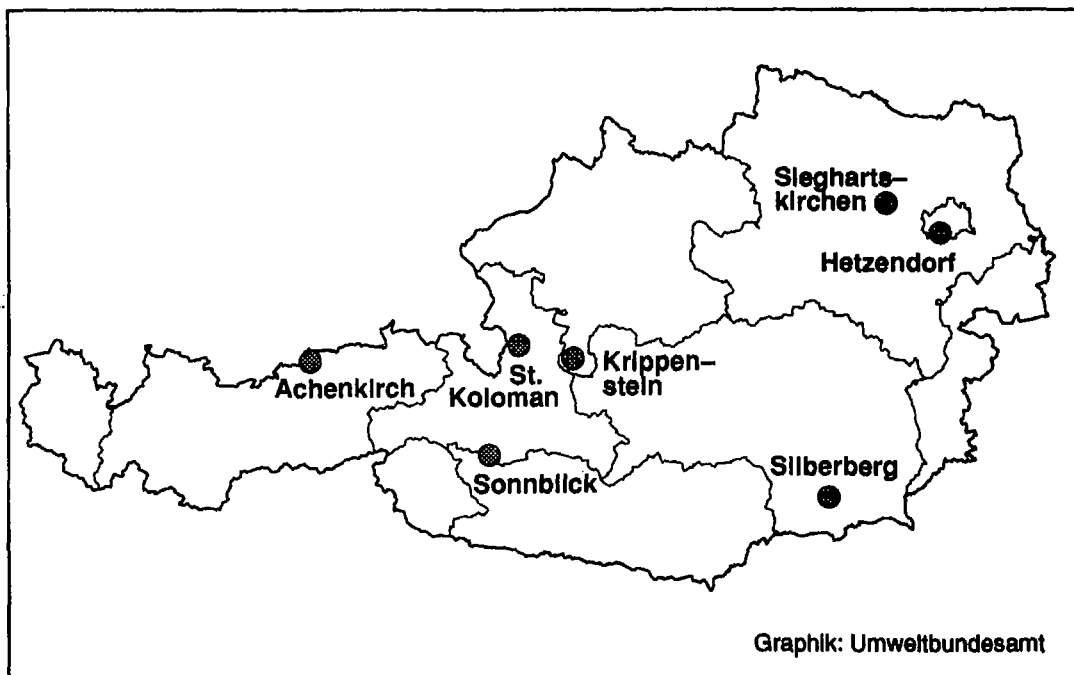
Introduction

Since the middle of 1991 the Federal Environmental Agency (Vienna, Austria) is carrying out a measuring programme for organic micropollutants in rain. Trichloroacetic acid (TCA) has been included into the analysis programme, firstly, because of its known phytotoxic behaviour and, secondly, because according to literature, TCA might develop from different precursor substances like 1,1,1 trichloroethane, tetrachloroethene, and trichloroethene by atmospheric photooxidation and radical decomposition.

In Austria the use of TCA as herbicide is prohibited by law since 1992.

Location and description of the sampling sites

At the following seven selected sites, situated in six Austrian provinces, rain water has been collected for a period of one month and analysed as mixed samples.



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Hetzendorf (Vienna):	suburban area in the south-west of Vienna
Sieghartskirchen (Lower Austria):	Intensively used agricultural area, south eastern part of the Tullner Feld, 205m
Silberberg (Styria):	Intensively used agricultural area in the western part of the Leibnitzer Feld, 300 m
Krippenstein (Upper Austria):	background station, in the region of the Dachstein, 2109 m
St. Koloman (Salzburg):	background station in Salzkammergut, 1008 m
Sonnblick (Salzburg):	alpine background station in the Central Alps, 3106 m
Achenkirch (Tyrol):	background station close to the German border, 820 m

Sampling

Rain sampling is done by a Wet And Dry Only Sampler (WADOS). The sampling vessels which are made of glass are changed daily in case of rain. The combined samples (one month, one site) are stored in darkness at 4°C prior to analysis.

Analysis

To 500 ml of the rain water sample 5 ml sulfuric acid (conc.) and 50 g sodium chloride are added. Extraction with 50 ml diisopropylether (DIPE) is carried out three times, the combined organic phases are dried over sodium sulfate. Then the drying agent is removed by filtering through glass wool, the volume carefully reduced to 1 or 2 ml and esterified by diazomethane solved in diethylether. The esterification is completed after 2 hours at room temperature. Then the volume of the extract is reduced to 1 ml by using a gentle stream of nitrogen.

At last 1-bromo-3-chloro-propane (dissolved in DIPE) is added as internal standard for gaschromatographic analysis. TCA is determined as TCA-methylester by EC-detection. Positive results are always verified by using a second capillary column of different polarity.

The recovery rate of the method is 74 % at a concentration level of 100 ng/l. The detection limit is 10 ng/l.

In order to obtain these data, a number of important factors have to be considered:

- The use of ground joints may cause losses of TCA.
- The amount of sodium sulfate should be minimized.
- The sodium sulfate has to be washed several times with diisopropylether.
- The reduction of the extract's volume must be carried out very carefully; complete evaporation of the solvent has to be avoided.
- All standard solutions are to be kept cool.
- The TCA-standard solution for spiking samples is used immediately after dilution.
- Esterification with diazomethane should be carried out in ethereal solution because the use of gaseous diazomethane (bubbling through the extract to be esterified) leads to losses of TCA.

GC-Conditions:

Instrument: HRGC 5300 (Fisons)

Column: a) DB 1301, 60 m, 0.32 mm I.D., 0.25 µm film thickness
b) 10 m precolumn, DX 4, 60 m, 0.32 mm I.D., 0.25 µm film thicknessTemperature programme: a) 40(5)/2/73/20/280(15)*
b) 50(1)/2/110/20/240(15)*Injection: 1 µl on column
secondary cooling: 15 secondsCarrier gas: a) He, 1.8 ml/min
b) He, 1.1 ml/minDetector: a) ECD, 290 °C
b) ECD, 255 °C**GC-MS-Conditions**

Instrument: GC 8065 (Fisons)/Trio 1000 (VG)

Column: 2 m precolumn;
PTE-5, 30 m, 0.25 mm I.D., 0.25 µm film thickness

Temperature programme: a) 40(5)/2/60/15/220(5)*

Injection: 1 µl on column
secondary cooling: 35 seconds

Carrier gas: a) He, 1 ml/min

Ions m/z: 117, 119, 121, 141, 143

Solvent delay: 4 minutes

Scanning time: 22 minutes

Measuring time: 0.08 seconds

Interchannel Delay: 0,02 seconds

Amu span: 0,1 amu

Ionisation: EI, 70 eV

Interface: direct capillary

Ion-source temperature: 180 °C

Interface temperature: 200 °C

* Data in °C and minutes: Start temperature (holding time)/rate 1 min⁻¹/end temperature 1 /rate 2 min⁻¹/end temperature 2 (holding time)**Results**

Trichloroacetic acid was found in all 85 analysed rain water samples. The concentrations ranged between 10 ng/l and 300 ng/l. The occurrence of this micropollutant at background stations (Achenkirch and St. Koloman at about 1000 m, Krippenstein at about 2000 m and Sonnblick at about 3000 m) is remarkable.

These results, which are in accordance with the relevant literature**, indicate the ubiquitous occurrence of TCA.

The results of TCA-analysis in rain water are graphically shown in figure 1. When no results are given, there was not enough water for analysis.

** Frank, H., Vincon, A., Reiss, J. (1990): Montane Baumschäden durch das Herbizid Trichloressigsäure. UWSF-Z., Umweltchem. Ökotox. 2(4): 208-214, Landsberg.

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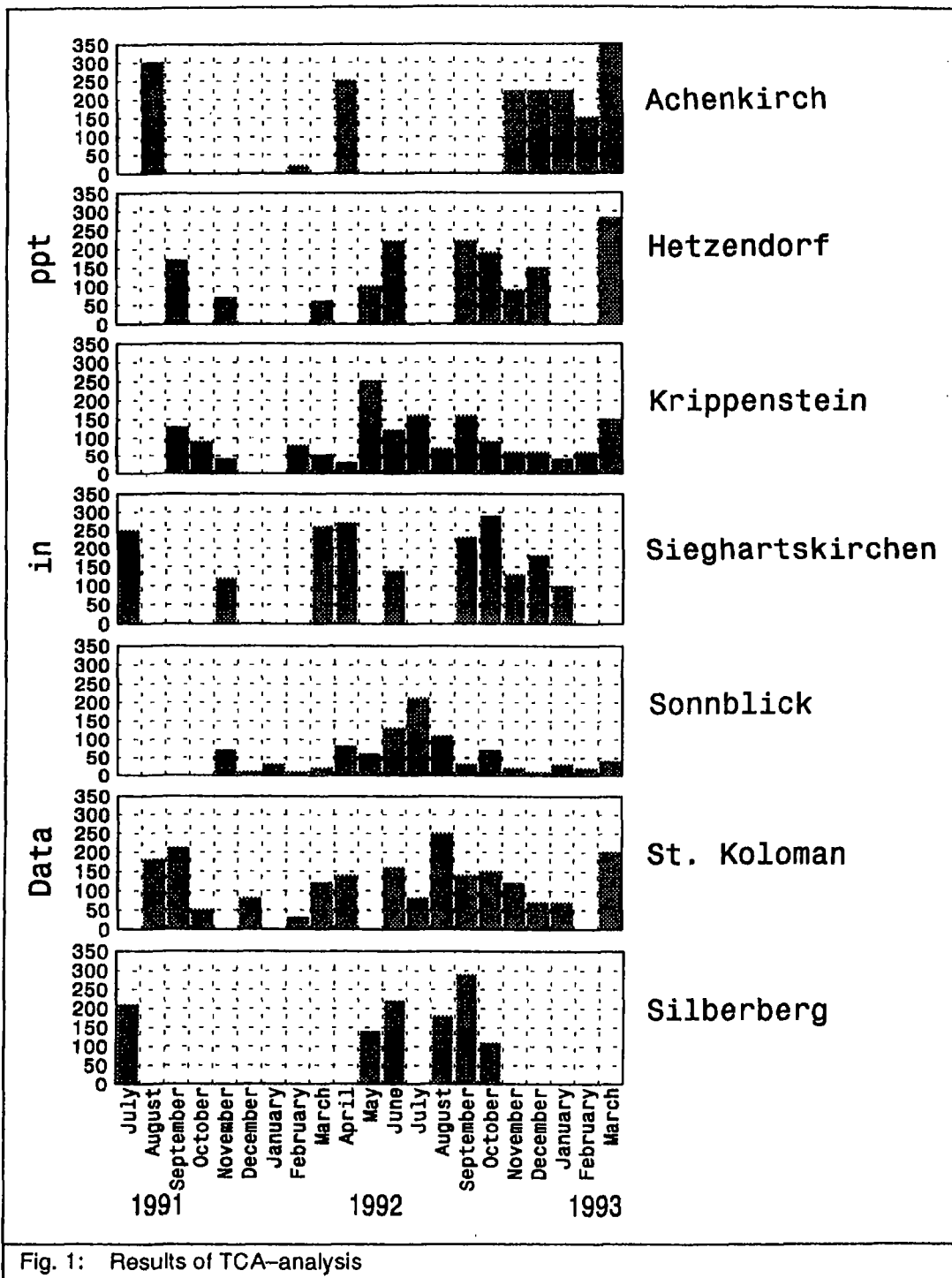


Fig. 1: Results of TCA-analysis