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# Trace Determinations of Individual Organic Pollutants – 25 Years of Research at the Swiss Federal Institute for Environmental Science and Technology (EAWAG)

Walter Giger\*

**Abstract.** An overview is given on analytical developments and applications for the determination of organic trace pollutants which have been performed at EAWAG since 1972. Gas and liquid chromatographic methods are of crucial importance. The presented examples include environmental hydrocarbons, semivolatile compounds and detergent-derived chemicals.

Until the late 1960's, the chemistry department of the Swiss Federal Institute for Environmental Science and Technology (EAWAG) performed mainly standard chemical analyses of waste waters, natural waters and drinking waters. This drastically changed after 1970 when the chemist Prof. *Werner Stumm* became EAWAG director. New chemical research included the determination of individual organic trace pollutants in the aquatic environment. The early 70's were an excellent time for such an endeavour because high-resolution chromatographic techniques using sensitive detectors and directly coupled methods such as GC/MS had become available. This article is a personal account on the activities at EAWAG during the last 25 years and on current research. The *Table* gives an overview of the research and development work carried out at EAWAG with respect to the determination of organic micropollutants. More detailed information including a compilation of publications is available on the internet [1]. Another CHIMIA report in this issue [2] and one article in the December 1997 issue [3] deal with trace organic analyses at EAWAG.

\*Correspondence: Prof. Dr. W. Giger  
Swiss Federal Institute for Environmental  
Science and Technology (EAWAG)  
CH-8600 Dübendorf

## Hydrocarbons in Recent Lake Sediments and the Fascination with Molecular Organic Geochemistry

In 1972 we were asked by the Canton Zug for consulting advice on the problems of the increasing number of small recreational boats on Lake Zug. This initiated investigations on hydrocarbons in recent lake sediments focusing on origins and fate of aliphatic, olefinic and polycyclic aromatic hydrocarbons (PAH). The appli-

cation of GC and GC/MS showed clearly that not all of the hydrocarbons found in the bottom sediments were of petroleum origin as had been postulated in an 'oil map' of the sediments of Lake Constance. It became evident that different sources were contributing such as biogenic production by phytoplankton, diagenetic synthesis after deposition, atmospheric inputs, surface runoff, erosion in the catchment area *etc.* Two representative results of PAH analyses in sediments (*Fig. 1*) clearly indicate the different origins of these sedimentary chemicals. Despite applying highly sophisticated analytical techniques such as  $^{14}\text{C}$  dating with accelerator mass spectrometry, no quantitative assignments to the various sources could be achieved. However, for PAH a large input through atmospheric depositions could be inferred. As a matter of fact, in the late 90's, PAH levels in soils are discussed in a similar way indicating that the source apportionment of environmental chemicals is an on-going question.

Until 1984 we published several articles in geochemically-oriented journals with emphasis on identifying individual organic molecules which became known under the term molecular fossils or biomarkers. We started to work at the interface between the anthroposphere with environmental chemicals and the geosphere with substances of geochemical origin. We were particularly impressed by the molecular analyses including stereochemical aspects carried out by the organic geochemists. Highly influential was the Swiss geochemist *Max Blumer*, doing research at the Woods Hole Oceanographic

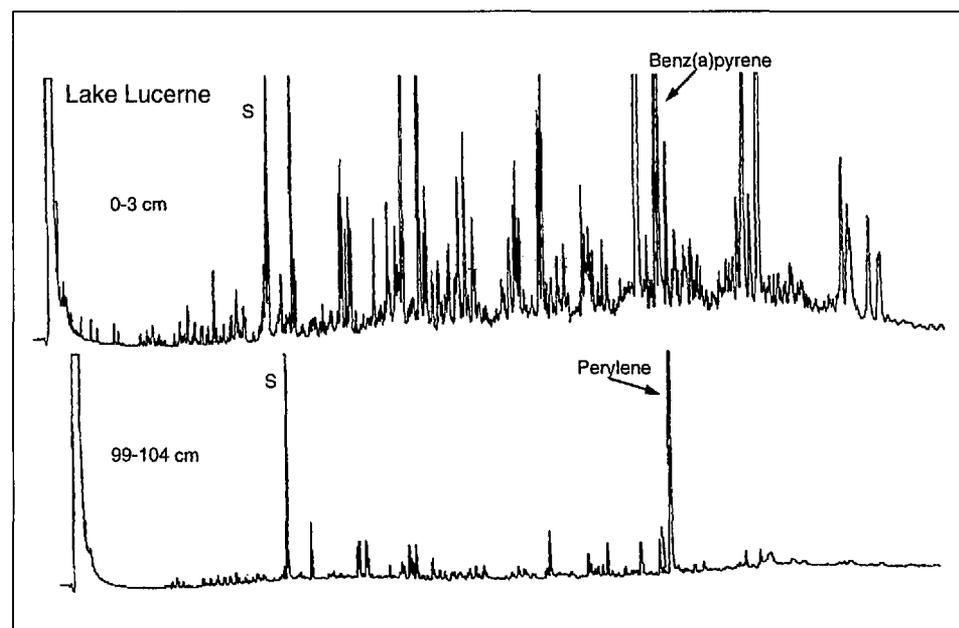


Fig. 1. Gas chromatograms of polycyclic aromatic hydrocarbons extracted from sediments of Lake Lucerne. In the surficial sediment mainly pyrolytic anthropogenic PAH are detected. Diagenetically (*i.e.*, after deposition) produced PAH predominate in the older sediments. S: standard compound.

Institution. The other very important tutor for us was Prof. *Kurt Grob* whose impact is described in the following chapter.

### The Grob Family – Glass Capillaries and Other Tools for High-Resolution Gas Chromatography

At the very beginning of our work on organic micropollutants we received very helpful advice from *Kurt Grob* who operated a GC laboratory and taught practical courses on glass capillary GC at the University of Zürich. In 1974 he moved his laboratory to our institute and became a focal point for many very important developments not only in high-resolution GC (HR-GC) using glass capillaries but also for sample treatment techniques such as the closed-loop gaseous stripping analysis (CLSA) for volatile trace organics in water. Researchers of EAWAG were often among the first testing new develop-

ments outside the inner circle of the *Grob* laboratory. The latter included besides *Kurt Grob* his wife *Gertrud*, the sons *Konrad* and *Matthias*, and the son-in-law *Joachim Schmid*. Today, many of the *Grobs'* developments are standard procedure in HR-GC. Just to name a few: splitless and on-column injection, direct aqueous injection, sample loops, chemically-bonded stationary phases and the *Grob* test for evaluating column performance. Fig. 2 shows two chromatograms obtained by packed-column and capillary GC, respectively. Almost 25 years later, this convincing comparison is still posted at the wall of a GC laboratory at EAWAG.

*Kurt Grob* received an international recognition also through his hands-on courses on HR-GC and trace organic water analyses. These so-called *Grob* courses were sponsored either by the Chemistry Department of ETH-Zürich or during many years by a European COST project (Cooperation Européenne Scientifique et Technique).

### Volatiles and Semivolatiles – Multimedia Analyses in Waste and Natural Waters

Using CLSA many EAWAG projects emphasized the fate of volatile organic compounds in the aquatic environment tracing their ways from sewage effluents via surface waters to ground water and drinking water. Key substances were substituted benzenes and naphthalenes and polychlorinated C<sub>1</sub>- and C<sub>2</sub>-hydrocarbons such as tetrachloroethene (perchloroethylene, PER). The latter chemical turned out to be an important, widely occurring contaminant of subsurface waters. In 1974, one of the first reports on an aquifer contaminated with PER was based on the results of water analyses obtained at EAWAG.

So-called semi volatiles were then studied in atmospheric depositions (rain, snow and fog) leading to the discovery of the widespread occurrence of nitrated phe-

Table. Milestones of EAWAG Research in Analytical Chemistry of Organic Pollutants

Year	Compounds	Analytical Method	Environmental System
1971–80	alkanes polycyclic aromatic hydrocarbons (PAH)	GC GC/MS	recent lake sediments
1974–84	volatile compounds polychlorinated volatile hydrocarbons	closed-loop gaseous stripping	surface waters groundwater
1980–85	polychlorinated phenols	derivatization	pulp mill effluents
1986–93	alkanes, PAH, phenols, nitrated phenols	rain/snow sampler	atmospheric deposition: rain, snow, fog
1980–	nonylphenol (NP)	HPLC with UV absorption or UV fluorescence	sewage effluents
1980–	nonylphenol polyethoxylates (NPEO)		sewage sludges
1983	nonylphenol polyethoxycarboxylates (NPEC)		mass balance studies in sewage treatment plants
1991–95	linear alcohol polyethoxylates (AEO)	high-temperature GC/MS	
1984–96	linear alkylbenzenesulfonates (LAS)	solid-phase extraction	accumulation and postdepositional behaviour in recent sediments
1991–94	secondary alkanesulfonates (SAS)	supercritical fluid extraction injection port derivatization	
1983–97	nitrilotriacetate (NTA)		surface waters
1985–97	ethylenediaminetetraacetate (EDTA)		
1988–97	ditallowdimethylammonium (DTDMAC)	HPLC with postcolumn derivatization	
1992–	fluorescent whitening agents (FWA)		
1991–	benzene- and naphthalenesulfonates (NBS)	solid-phase extraction with graphitized carbon black	industrial wastewater landfill leachates
1989–	tributyltin (TBT), tinorganics		harbour sediments
1990–	triazines (atrazine, metabolites)		
1993–	haloacetic acids		

nols (Fig. 3). The concept of dividing the samples in particulate and aqueous phases provided valuable information on the environmental behaviour of various compound classes such as anthropogenic and biogenic alkenes, PAH and phenols.

### Detergent Chemicals – From Monitoring to Process-Oriented Field Studies

Chemicals contained in laundry and cleaning products have long been problematic substances with regard to their fate in wastewater treatment and effects in the aquatic environment. For many years they were analytically determined by non-specific methods because of their complex product compositions. With the progress of specific analytical methods it became feasible to measure many of these detergent ingredients individually. The EAWAG laboratory for organic analysis played a key role as one of a few nonindustrial research groups. One major advantage of the EAWAG involvement was based on the close cooperation with engineers, microbiologists and earth scientists. Specific environmental analytical methods have been developed for several detergent chemical compound classes (see Table). These methods were applied for mass balance and process-oriented field studies in different compartments of the aquatic environment including sewage and sewage sludge treatment, surface and sub-surface waters [4][5].

The selective determination of the aromatic surfactants linear alkylbenzenesulfonates (LAS) and nonylphenolpolyethoxylates (NPEO) could be achieved by HPLC (Fig. 4). Based on the results of the EAWAG studies, the risk assessment was re-evaluated for these two high-volume chemicals.

Consequently, in 1986 the use of NPEO for laundry washing was banned in Switzerland and in several other countries these chemicals were largely phased-out by the manufacturers [6]. In other cases of water pollution control measures, e.g., the phosphate ban in laundry detergents, the organic analytical group of EAWAG has been essential for the environmental monitoring of nitrilotriacetate (NTA), a disputed phosphate substitute.

### Current and Future Projects

Nowadays, in the late 1990's, many governmental and private laboratories are carrying out determinations of trace or-

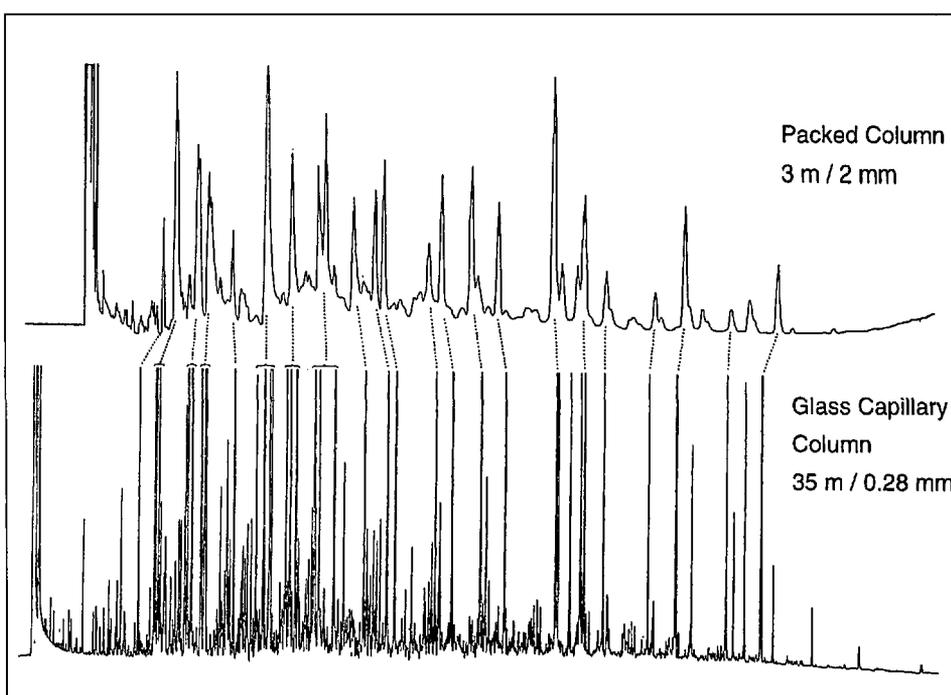


Fig. 2. Gas chromatograms with packed and capillary columns. An extract from a water sample of the Glatt river is analyzed.

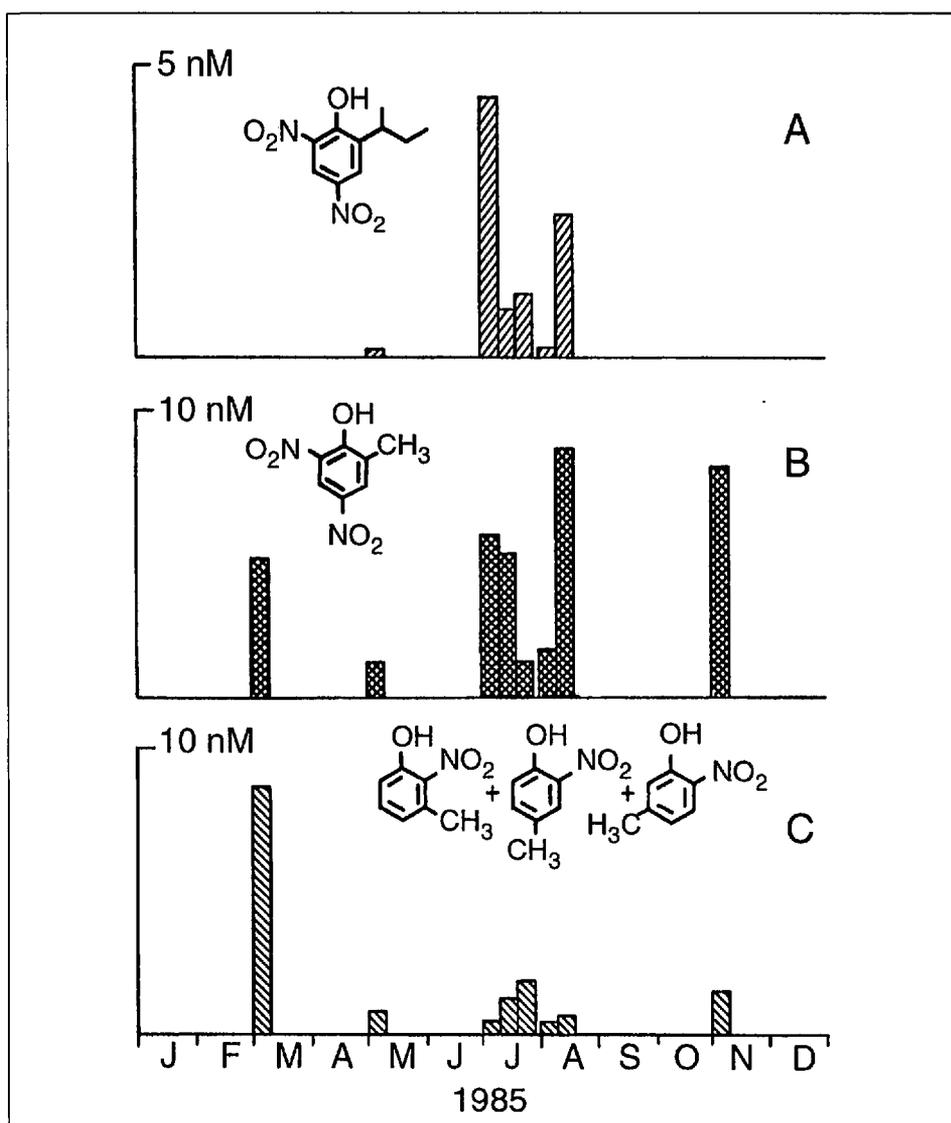


Fig. 3. Nitrated phenols in rain water. The seasonal variation of compound A indicates a specific input from agricultural use. The other nitrated phenols are assigned to nonspecific sources.

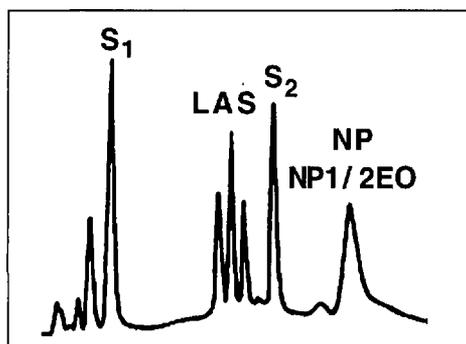


Fig. 4. HPLC Determination of linear alkylbenzenesulfonates (LAS) and nonylphenol polyethoxylates (NP, NP1EO, NP2EO). S<sub>1</sub>, S<sub>2</sub>: standard compounds.

ganic environmental pollutants. Most of them are primarily active in monitoring programs of different types aiming at observing spatial and temporal differences in environmental quality. In contrast, the strength of current EAWAG projects are based on the following aspects:

- Interdisciplinary co-operation with biologists, engineers, earth scientists, mathematical modelers and environmental physicists;
- Process-oriented field studies in order to understand the important environmental fate mechanisms;

- Freedom of selecting 'nontarget' analytes which are not or not yet included in routine monitoring.

We are currently involved in developing and applying analytical methods for a large number of environmental chemicals. We are particularly focusing on amphiphilic and hydrophilic pollutants in contrast to the large amount of work done on the more volatile and lipophilic pollutants. Some of our main analytes are listed below:

- Benzene- and naphthalenesulfonates as widely occurring highly hydrophilic pollutants in industrial wastewaters and in leachates from landfills;
- Concrete admixtures (superplasticizers): naphthalene- and melamine-sulfonate formaldehyde condensates;
- Fluorescent whitening agents and cationic surfactants (ditallowdimethylammonium chloride, DTDMAC) from laundry detergents;
- Sulfophenyl carboxylates (LAS metabolites): separation of the enantiomers by CZE;
- Antibiotics in hospital waste waters (e.g., Ciprofloxacin);
- Endocrine disrupting chemicals (environmental hormones): nonylphenol in

digested sewage sludges and in natural waters.

Overall, there is still ample opportunity to develop analytical methods using most advanced techniques (e.g., MS/MS, LC/MS, CZE) to unravel the environmental fate of relevant organic pollutants. In the future, we intend to more strongly emphasize the combination of chemical and biological analyses. As in the past we will be involved in national and international activities funded by private and governmental sources including the research and development program of the European Union. We believe that our research results will continue to be used as part of the decision making for environmental protection measures, be it by legislation or by manufacturing environmentally safer chemical products.

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## Analytik im Dienst der landwirtschaftlichen Umweltforschung

Heinz Häni\*

### Analytical Chemistry as Means of Agricultural Environmental Research

**Abstract.** Research in agricultural environmental protection strongly depends on efficient, appropriate and versatile analytical instrumentation. In the present paper the main interest is concentrated on the determination of the concentration of inorganic and organic pollutants in solids (mainly soils) and the analysis of trace gases in air (including the study of photochemical oxidation, e.g., formation of ozone). Due to the heterogeneity of solids and the many steps from sampling to measurement, great importance is paid to the analysis of chemical laboratory data by proficiency tests. Analytical data are used for monitoring pollutants in the environment as a basis for regulatory action, and as an indicator of their impact.

### 1. Einleitung

In der landwirtschaftlichen Forschung gewinnen Umweltfragen zunehmend an Bedeutung, d.h. die Rolle der Landwirt-

schaft als Opfer und als Verursacherin von Umweltbelastungen steht im Vordergrund. Speziell im Hinblick auf eine mögliche Gefährdung von Boden, Wasser und Luft befasst sich das Institut für Umweltschutz

und Landwirtschaft im Liebefeld (IUL), das Teil der Forschungsanstalt für Agrarökologie und Landbau mit Hauptsitz in Zürich-Reckenholz (FAL) ist, mit der Früherkennung landwirtschaftlicher Umweltprobleme. Zur Aufstellung von Prognosen werden Ursachen und Wirkung der Belastungen (hauptsächlich durch Schadstoffe) erforscht. Schliesslich wird nach Wegen gesucht, die stoffliche Belastung von Boden, Wasser und Luft zu vermindern.

Nicht zu vergessen sind die Vollzugsaufgaben, die das IUL im Zusammenhang mit der Umweltschutzgesetzgebung wahrzunehmen hat. Es sei dabei vor allem auf die Verordnung über umweltgefährdende Stoffe (StoV) und die Verordnung über Schadstoffe im Boden (VSBo) verwiesen.

Zur Lösung all dieser Aufgaben ist eine leistungsfähige Analytik in den verschie-

\*Korrespondenz: Dr. H. Häni  
Eidgenössische Forschungsanstalt  
für Agrarökologie und Landbau  
Institut für Umweltschutz und  
Landwirtschaft (IUL)  
Liebefeld  
CH-3003 Bern