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Behaviour of polycyclic aromatic hydrocarbons (PAHs) and triazine herbicides in water and aquifer material of a drinking water recharge plant

I. The area of investigation and the determination methods for PAHs and triazine herbicides in the aqueous matrix

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Summary. On the background of a discipline overlapping research project of the "Deutsche Forschungsgemeinschaft" (DFG), entitled: Pollutants in ground water, the behaviour of PAHs and triazine herbicides during the water gathering process by means of underground passage was investigated. The publication is divided into four parts (I–IV). In the present part the area of investigation including the monitoring network and the determination methods for PAHs and triazine herbicides in the aqueous matrix are described.

1 Introduction

In the last century increasing consumption and limited resources of natural ground water led to the development of methods for the production of drinking water by bank filtration. In 1980 nearly 45% of the drinking water in North Rhine Westfalia was developed from surface water [1].

The concentrations of pollutants in the surface water used for the production of drinking water must be reduced during the underground passage to achieve a sufficient drinking water quality.

According to the German Drinking Water Decree the limit value for the sum of six polycyclic aromatic hydrocarbons (PAH) is provided with 200 ng/l, the limit value for pesticides is 100 ng/l for individual pesticides and 500 ng/l for their sum [2].

In the course of the study presented the behaviour of PAH and triazine herbicides during the water gathering process by means of underground passage was investigated.

Long-term investigations of the ground water were carried out in the time from November 1987 till June 1990 in several areas of the drinking water recharge plant (artificial recharge of ground water) as well as in the river Ruhr.

2 Area of investigation

The drinking water gathering plant Hengsen of the town's department of works (Stadtwerke Dortmund) is situated in the Ruhr valley near Dortmund. The work facilities are the barrage lake, the intake structure, six primary filter basins, three main filters and the drainage pipe [3] (see Fig. 1).

The barrage lake is supplied with water by a feeding channel from the Ruhr which is dammed by a weir in this area. The water which is not used for the drinking water development flows back to the river bed through the tail race.

Through the intake structure the barrage lake water is led to the primary filter basins. They are filled with coarse gravel and sealed with a layer of compacted loam of 30 cm thickness in the direction to the aquifer. From this point the primary filtrate flows through pipelines to the main filters (slow sand filters) which are filled with a sand layer of 0.5–0.7 m thickness. They are open in the direction to the aquifer. The artificial infiltration water flows into the direction of the drainage pipe. The withdrawal of the purified water occurs in this drainage pipe which lies in parallel to the main filter basins 2 and 3. The pipe is coupled with the water gathering plant Lappenhausen, thus the conveyed water is a mixture of two infiltrates (Hengsen/Lappenhausen).

Without the influence of the operation of the waterworks there is a ground water flow from the barrage lake in direction to the Ruhr. This current is caused by the potential difference of about 5.5 m between the barrage lake and the natural course of the Ruhr. Normally, the natural ground water flow is overlaid by the operation of the waterworks. An artificial enrichment of ground water by means of the slow sand filters basins (main filter basins) increases the potentials of the ground water under these basins. This leads to a displacement of the bank filtered water which is infiltrated from the barrage lake.

During the conveyance of ground water from the drainage pipe a ground water flow of artificial infiltration water is formed from the direction of the main filters, bank filtrate is formed from the direction of the barrage lake and both flow into the direction of the drainage pipe. The recharge is the quantity of water to be loaded onto the main filters per unit of time. The conveyed and recharged quantities can be calculated from the pump operating data. The hydraulic

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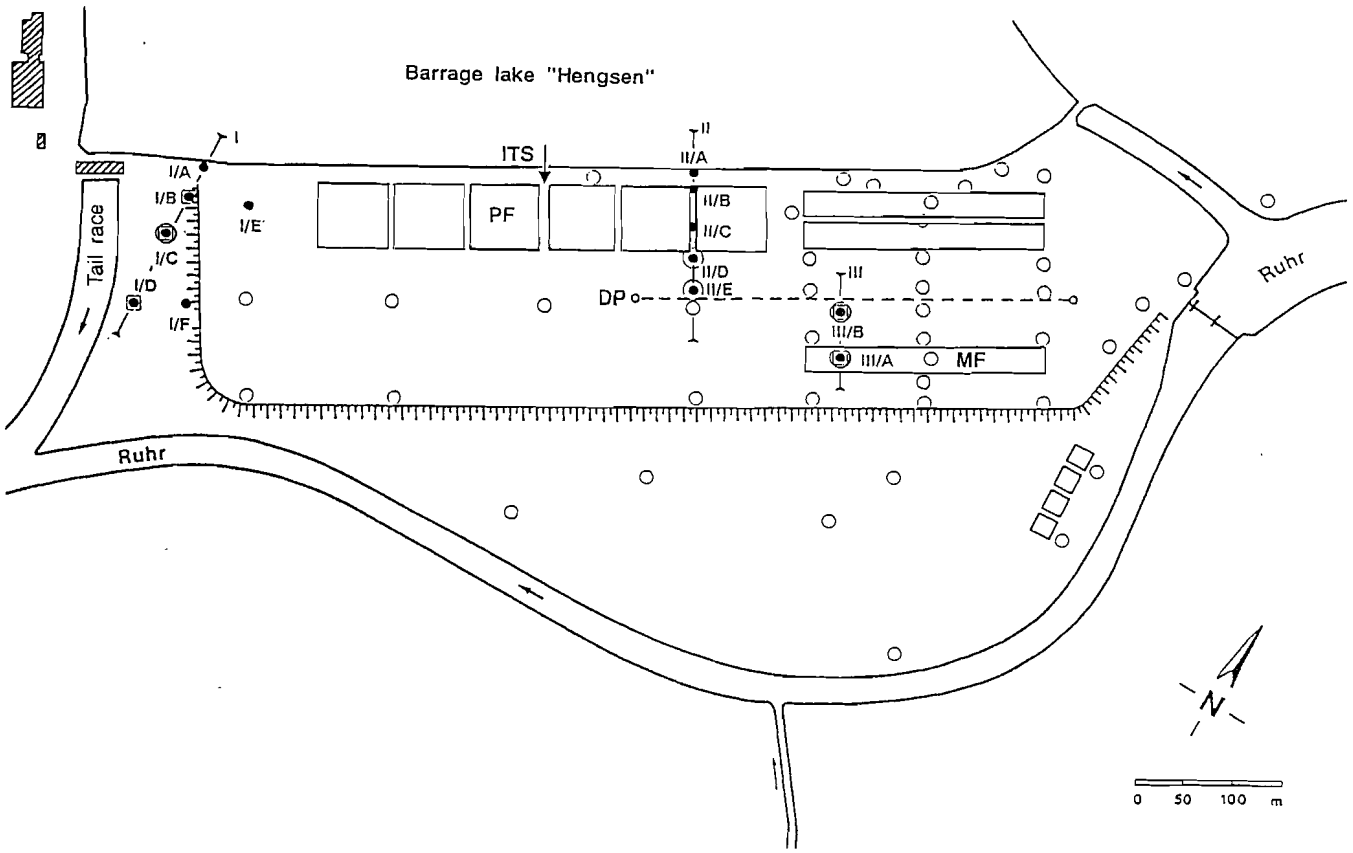

Fig. 1. The water recharge plant including the work facilities. *ITS*: Intake structure; *PF*: Primary filter; *MF*: Main filter; *DP*: Drainage pipe; Wells of the transects: (I/A – I/D), (II/A – II/E), (III/A – III/B)

state in the underground and the quality of the water can be controlled by use of these two operational parameters.

2.1 The transects

The area of investigation of the water recharge plant is subdivided into three transects which are nearly in parallel to the flow-pathways of the ground water (see Fig. 1). The wells constructed in this area are built of polyvinyl chloride or stainless steel pipes (5 cm internal diameter) which are equipped with filters of a defined size at their bottom. Every measuring point in the transects consists of several wells of different depths. For the routine sampling, the water samples were always taken from the same well at the respective measuring point (see Table 1). The measuring depths as given in Table 1 refer to the top edge of the well.

2.1.1 Transect I. In transect I the water flows from the barrage lake to the south-west direction to the tail race. Four measuring points, I/A to I/D, are installed along the transect. The transect I is not influenced by the water plant with its different hydraulic operation conditions. The flow velocity of the oxygen-poor bank filtrate in the underground is low (approx. 0.2 m/d [4]). Anaerobic conditions are found in transect I. The surface water levels in the barrage lake and in the tail race show backwater effects in particular under extreme conditions. During flood water events for example, the water gauges within transect I increase and the water flow is slower in the direction of the tail race.

2.1.2 Transect II. Transect II (measuring points II/A to II/E) lies in parallel to the ground water flow which is developed from the barrage lake to the drainage pipe. In the upper area of transect II (II/A, II/B, II/C) the ground water mainly consists of oxygen-poor bank filtrate (anaerobic conditions); the ground water in the measuring points II/D and II/E consists of oxygen-rich artificial infiltrate from the main filters (aerobic conditions) whereas the relation between both depends on the hydraulic conditions of the waterworks. A high accumulation rate of artificial filtrate on the main filters for example leads to decreasing contents of bank filtrate with changing redox potentials at the measuring points II/C and II/D and changing flow velocities in the transect (0.2 – 2.5 m/d [4]). The respective quantity of recharge and conveyance is adapted to the requirement of the waterworks and therefore it depends on the daily fluctuations.

2.1.3 Transect III. Transect III is in parallel to the flow of the ground water from the main filter basin to the direction of the drainage pipe. The ground water in transect III only consists of oxygen-rich artificial filtrate (aerobic conditions) which depends directly on the hydraulic conditions of the waterworks. Two measuring points (III/A and III/B) are located in transect III. The main filter 3 is alternately operated with the main filters 1 and 2. As a consequence a flow of ground water is only developed from III/A into the direction III/B, if the main filter basin 3 is loaded with water and if a conveyance from the drainage pipe occurs. The high oxygen content of the artificial filtrate is due to the water

Table 1. Measuring points and depths of the routine sampling during the long-term investigations

	Measuring point		Sampling depth [m]
	Name	Number of the well	
Transect I	I/A	1	7.0
	I/B	2	6.5
	I/C	5	6.0
	I/D	1	6.5
Transect II	II/A	1	7.0
	II/B	1	7.0
	II/C	1	6.5
	II/D	1	6.0
	II/E	1	5.0
Transect III	III/A	4	4.0
	III/B	4	5.0
	Ruhr		1 m below the water level
Additional measuring points	ITS		1 m below the water level
	PF		1 m below the water level
	MF		1 m below the water level
	DP		

ITS: Intake structure part; PF: Prefilter; MF: Main filter; DP: Drainage pipe

passage in this transect leading through several cascade systems. The flow velocity of the water is fast with 2.5 m/d [4].

2.2 The drainage pipe (DP)

The ground water conveyed by means of the drainage pipe is the output of the water recharge plant. It is a mixture of bank filtrate, artificial infiltration water and ground water from the water recharge plant Lappenhausen.

2.3 The river Ruhr

The water of the river Ruhr is the input of the water recharge plant. The samples were taken from the feeding channel.

2.4 Additional measuring points

In the course of the time the network of measuring points was extended (see Table 1). Further samples were taken from the intake structure part (ITS) the primary filter inlet (PF) and the main filter inlet (MF) (see Table 1).

3 Routine sampling

The routine sampling was carried out in a two-weekly interval from November 1987 till April 1990 (PAH) and from May 1988 till June 1990 (triazine herbicides). The samples were taken from the Ruhr and from the wells at the measuring points of the three transects. Later the sampling procedure was extended so that additional measuring points within and outside of the transects were established (see Table 1).

Samples were taken by means of an immersion pump which operated with a 12 V battery (exception: measuring point DP). The water sample was taken after the clear-point

Table 2. List of quantified and investigated substances

IUPAC Name	Abbreviation	Molecular weight
Anthracene	Ant	178
Fluoranthene[a]	Fla	202
Pyrene	Pyr	202
Benz(a)anthracene	Baa	228
Chrysene	Cry	228
Benzo(b)fluoranthene[a]	Bbf	252
Benzo(k)fluoranthene[a]	Bkf	252
Benzo(a)pyrene[a]	Bap	252
Dibenz(a,h)anthracene	Dba	252
Benzo(ghi)perylene[a]	Bgh	276
Indeno(1,2,3-cd)pyrene[a]	Ind	276

[a] PAH which have to be quantified according to the German Drinking Water decree

but earliest after a minimum pumping time of 5 min. Thus the PAHs adsorbed at the suspended matter are collected too. Preliminary experiments and check tests were performed with respect to the influence of the pumping time on the PAH concentration. It could be demonstrated that the PAH content of the water sample is stable after 5 min of continuously pumping; 1043 ml of the water sample were collected in a brown glass bottle. To avoid adsorption effects of the PAHs at the glass surfaces, 100 ml 2-propanol (8.75%) were added directly during the sampling. The samples were only stored for several hours until their preparation.

A differentiation of the PAH concentration by depth in the aquifer was not detected. Thus the sampling intake locations could be regarded as representative.

The water samples for the triazine herbicide investigations were taken simultaneously in a similar manner, an addition of 2-propanol was not necessary in this case.

4 PAH determination in ground water and surface water

For the determination of PAHs in aqueous matrices a sample preparation is required which effects an enrichment of the analytes, because their real concentrations in water are normally below the detection limit of the analytical method. Due to the low stability of the PAHs in the water samples, samples must be treated rapidly and in parallel. A practicable, rapid and reliable sample preparation is achieved by use of an optimized solid-phase extraction on a conventional C-18 cartridge [5].

For the separation, detection and quantification of the 16 PAHs (EPA standard) a selective and sensitive analytical method is required. For this purpose a high performance liquid chromatographic (HPLC) method with time programmed fluorescence detection is applied.

4.1 Chemicals

Dichloromethane, nanograde; 2-propanol, nanograde; cyclohexane, nanograde; 3,6-dimethylphenanthrene and the 16-PAH standard SRM 1647a were obtained from Promochem (Wesel, Germany); HPLC-grade acetonitrile and Adsorbex Amino cartridges, 400 mg, were from Merck (Darmstadt, Germany). Bakerbond SPE – C-18 cartridges, 1000 mg, Nr.: 7020-07; Bakerbond SPE – Amino car-

tridges, 500 mg, were obtained from Baker (Groß-Gerau, Germany). HPLC-grade water was generated by use of a Milli-Q-Reagent Water System from Millipore (Eschborn, Germany). All other chemicals were of the highest purity obtainable.

4.2 Instrumentation

The HPLC system consisted of a Model L-6200 gradient pump, a Model 655A-40 autosampler, a HPLC Manager Interface and Software D-6000 from Merck (Darmstadt, Germany); a reversed-phase column: Bakerbond Wide Pore, C-18, 5 µm, 250 × 4.6 mm i.d. from Baker (Groß-Gerau, Germany); a fluorescence detector LS-4 from Perkin Elmer (Überlingen, Germany); a column oven TC 831 from HPLC Technology and an IBM-AT compatible computer, 640 KByte RAM, 40 MByte Winchester.

4.3 Sample preparation

Before solid-phase extraction, the combination of aminopropyl (NH_2) and octadecyl (C-18) solid phase cartridges is conditioned with 3 ml cyclohexane, 3 ml dichloromethane, 3 ml 2-propanol and 3 ml 2-propanol/water (8.75/91.25, v/v).

Then the stabilized water samples (1043 ml, stabilized with 100 ml 2-propanol, cf. chapter 3) are sucked in parallel each through a silicone tubing over the combination of the cartridges by means of water jet vacuum. The dropping velocity is 1 – 2 drops per second completing the extraction procedure in about 7 h. The glass bottle is rinsed with a few milliliters of a mixture of 2-propanol/water (8.75/91.25, v/v) which are added on the upper cartridge (NH_2-cartridge). After the cartridge-system is sucked until dryness (approx. 5 min with air) it can be stored at −20° C or it can be directly eluted.

The combined cartridges are separated before elution but the eluates of the cartridges are collected in one 2 ml volumetric flask. Each of the following elution steps has a duration of exposure of 10 min. Each of both cartridges is eluted twice with 1 ml dichloromethane and once with 0.5 ml dichloromethane. The dichloromethane is concentrated in a stream of nitrogen and for the aminopropyl cartridge the elution procedure is repeated. The collected dichloromethane is completely blown off in a stream of nitrogen under addition of 1 ml acetonitrile (to avoid complete dryness). The volumetric flask is filled up to 2 ml with acetonitrile under addition of 200 µl dimethylphenanthrene solution (internal standard; 440 ng/ml). The thus prepared extract is transferred into autosampler vials and analyzed by HPLC.

4.4 Chromatography

For the analysis of the 16 PAHs a given HPLC-separation [5] was modified to be suited for the special demands as a routine analysis of real samples. The separation is achieved on a reversed-phase column with acetonitrile/water. The gradient is as follows: 5 min acetonitrile/water 45/55, v/v; a linear gradient to 100% acetonitrile in 24 min; these conditions are hold for 6 min. The starting conditions are reached again in 7 min, the column is equilibrated at these conditions for 8 min. The column temperature is 37° C, the flow 1.3 ml/min, the injection volume is 20 µl.

Table 3. Time program of the fluorescence detector for the quantification of PAHs in water

Time [min]	Excitation [nm]	Emission [nm]
0	270	333
11	250	345
16	240	425
22	265	380
25	290	410
32	300	502
35	270	333

Band width of the excitation wavelength: 10 nm
Band width of the emission wavelength: 15 nm

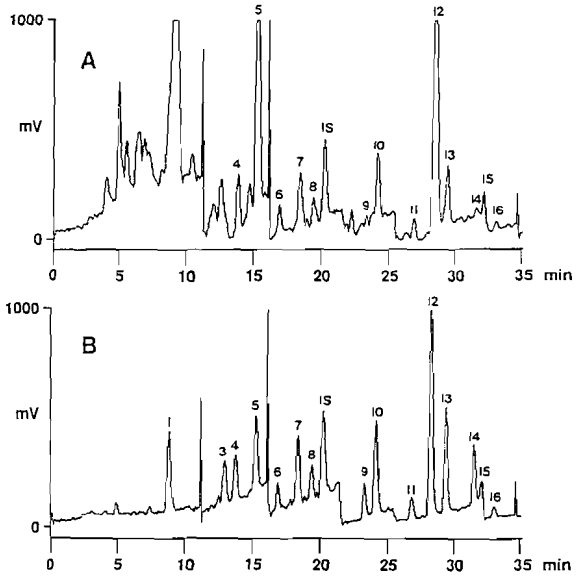

Fig. 2. A Chromatogram of a water sample (Ruhr); **B** chromatogram of a PAH-standard containing 16 PAHs (SRM 1647a, 7 – 50 pg). *1* Naphthalene[a]; *2* Acenaphthylene[a]; *3* Acenaphthene[a]; *4* Fluorene[a]; *5* Phenanthrene[a]; *6* Anthracene; *7* Fluoranthene; *8* Pyrene; *9* Benz(a)anthracene; *10* Chrysene; *11* Benzo(b)fluoranthene; *12* Benzo(k)fluoranthene; *13* Benzo(a)pyrene; *14* Dibenz(a,h)-anthracene; *15* Benzo(g,h,i)perylene; *16* Indeno(1,2,3-cd)pyrene; IS 3,6-Dimethylphenanthrene; [a] These substances could not be quantified

A selective and sensitive detection of the PAHs was performed by using time programmed switching of the excitation and emission wavelengths. The desired wavelength conjugation for the individual substances was selected on the basis of literature spectra [6 – 8]. The time program of the fluorescence detector with the excitation and emission wavelengths is given in Table 3.

The application of an internal standard was needed for the automated peak detection. 3,6-dimethylphenanthrene (DMP) is well suited for this purpose and therefore it was added to the calibration standards and to each HPLC sample (Fig. 2).

4.5 Reliability of the method

The characteristic data for the investigated PAHs are mainly parameters which describe the efficiency of the complete

Table 4. Characteristic data for the determination of PAHs in water

Substance	Medium of the investigated concentration range [ng/l]	Standard deviation of the method [%]	Recovery [%]	Determination limit [ng/l]
Anthracene	0.77	9.41	69.2	0.33
Fluoranthene	7.68	10.87	72.0	1.93
Pyrene	8.25	6.83	70.7	2.73
Benz(a)anthracene	3.82	11.05	78.9	1.29
Chrysene	3.62	11.27	86.2	0.35
Benzo(b)fluoranthene	4.08	11.16	92.1	0.95
Benzo(k)fluoranthene	4.61	8.48	85.9	0.15
Benzo(a)pyrene	4.82	10.25	77.9	0.28
Dibenz(a,h)anthracene	3.72	9.17	85.0	0.21
Benzo(ghi)perylene	3.75	10.02	79.0	0.70
Indeno(1,2,3-cd)pyrene	4.32	9.52	85.4	1.02

determination method including the HPLC (see Table 4). The determination of the relative standard deviation of the method was in accordance with the method of the calibration curve [9] and the determination limit was calculated in correspondance with the method of the blank [10].

4.6 Test of matrix influence

Different matrices can influence the measured values so that a distortion may result. This is possible in case of the PAHs, because its hydrophobic character leads to an adsorption at the suspended matter. Therefore it is evident that water containing different quantities of suspended matter can show methodical errors [11].

For this reason the influence of the different waters in the area of investigation on the PAH-determination had to be tested. This test was carried out by comparing the slopes of the calibration curves in distilled water with those functions obtained by applying the addition (spiking) method on different waters of the area of investigation by means of statistical methods [12].

The validity of the developed analysis method for the determination of PAHs in water concerning the matrix of the investigated area as well as for distilled water was established on the basis of these tests.

4.7 Summarized valuation of the method

The developed and optimized method for the determination of PAHs in water permits the quantification of 11 substances of the 16 PAHs in the EPA standard (see Table 2). It is possible to apply the analysis method as a routine by investigating a great number of water samples in parallel whereas the sample output rate is only limited by the HPLC analysis time.

The characteristic operational steps of the method are:
- Stabilization of the sample with 2-propanol to avoid wall adsorption of the PAHs,
- Solid phase extraction of the PAHs by use of a plug-in combination,
- Elution of the analytes with dichloromethane,
- HPLC analysis with fluorescence detection.

5 Determination of triazine herbicides in ground water and surface water

An analysis method had to be developed or an existing method had to be optimized to study the behaviour of triazine herbicides during their underground passage. The method should show the following performance characteristics:
- Working range from 10 – 1000 ng/l,
- Selectivity for the agents to be investigated,
- Determination of the most important metabolites (desalkyl derivatives and hydroxyl derivatives),
- Preparation of up to 20 samples in parallel,
- Applicable as a routine by a low personal expenditure,
- Reproducibility,
- Sufficient precision.

5.1 Chemicals

Triazine herbicides and metabolites as well as HPLC-grade methanol were obtained from Promochem (Wesel, Germany). HPLC-grade acetonitrile, potassium dihydrogenphosphate, suprapur, potassium hydroxide, suprapur and Adsorbex Amino cartridges, 400 mg were from Merck (Darmstadt, Germany). Bakerbond SPE – C-18 cartridges, 1000 mg were from Baker (Groß-Gerau, Germany). HPLC-grade water was generated by use of a Milli-Q-Reagent Water System from Millipore (Eschborn, Germany). All other chemicals were of the highest purity available.

5.2 Instrumentation

The HPLC-system consisted of a Model L-6200 gradient pump, a column LiChrospher 60, RP-select B, 5 µm, 250 × 4 mm; a Model 655A-40 autosampler, a Model L-4000 UV-detector, a Model L-3000 diode array detector coupled with PC/AT and an integrator D-2000. The modular units of the HPLC-system were obtained from Merck (Darmstadt, Germany).

5.3 Sample preparation

To be able to determine plant protective agents in water samples in the desired concentration range from 10 to

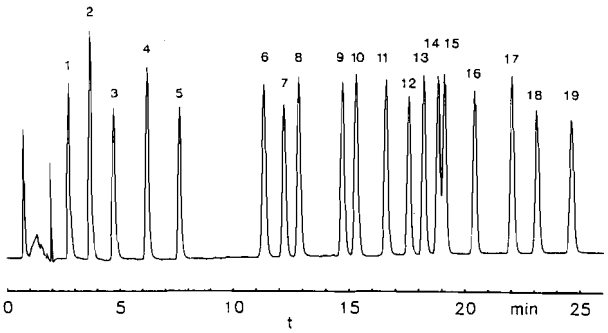

Fig. 3. Chromatogram of a triazine herbicide standard. *1* Hydroxysimazine; *2* Desisopropylatrazine; *3* Hydroxyatrazine; *4* Desethylatrazine; *5* Hydroxypropazine; *6* Simazine; *7* Cyanazine; *8* Atratone; *9* Desmetryne; *10* Atrazine; *11* Prometone; *12* Methoprotryne; *13* Terbumetone; *14* Sebutylazine; *15* Propazine; *16* Terbutylazine; *17* Prometryne; *18* Terbutryne; *19* Dimethametryne

1000 ng/l, an enrichment of these agents is required. The concentrating procedure is carried out by means of solid-phase extraction on C-18 modified silicagel. In this way a great number of samples can be treated in parallel and the recovery of polar metabolites and agents is better than for liquid/liquid-extraction.

Mainly in the case of surface water samples a strong increase of the baseline at the chromatogram start and end is observed, if the cartridges are extracted with methanol and analyzed by HPLC without a clean-up procedure. To improve the detectability and to avoid contamination of the separating column it was necessary to introduce a clean-up step. The clean-up step should be simple to realize and it should not influence the recovery of the analytes. Therefore the clean-up step was included in the elution procedure. This is possible due to the coupling of the concentrating cartridge with an amino cartridge which retains the undesired accompanying substances.

Before the sample preparation, the cartridges are conditioned each with 2×3 ml methanol and with 2×3 ml bidistilled water. After that 1000 ml of the water samples are sucked in parallel each through a glass tubing over the C-18 cartridge by means of water jet vacuum with a flow rate of approx. 4–5 ml/min. The loaded cartridge is washed with 3×3 ml bidistilled water and dried by sucking air over it for 5 min. For the elution of the enriched analytes the cartridge is fixed on the conditioned aminopropyl cartridge and the cartridge combination is eluted with 2×0.75 ml methanol and with 2×0.5 ml methanol. Each elution step has a reaction time of 20 min. The eluates are collected in a 1 ml volumetric flask and concentrated in a stream of nitrogen below a volume of 0.75 ml. Then 0.25 ml buffer (0.001 mol/l KH_2PO_4, pH 7.0) are added, the solution is filled up to 1 ml with methanol and transferred to an autosampler vial.

5.4 Chromatography

A HPLC-method is developed because it offers the possibility to determine the extreme polar hydroxy metabolites and thermolabile agents without particular chemical conversion [13, 14–16]. The separation was optimized to permit the simultaneous separation of active agents as well as some hydroxy and desalkyl metabolites [17, 18].

To achieve a short analysis time at a sufficient separation efficiency (baseline separation if possible) the application of gradient elution with acetonitrile/0.001 mol/l KH_2PO_4 is necessary. The gradient is as follows: A linear gradient from 22% to 58% acetonitrile in 24 min and from 58% to 100% acetonitrile in 3 min. These conditions are held for 8 min, the starting conditions (acetonitrile/buffer, 22/78, v/v) are reached again within 2 min and the column is equilibrated at these conditions for 7 min. The flow is 1.5 ml/min, the injection volume is 100 µl.

Applying this method, the triazine derivatives could be separated in about 25 min (see Fig. 3). The total time for one separation run including the equilibration is 44 min.

The triazine herbicides are detected and quantified using UV-detection at 220 nm. To confirm the identification of detected substances in real samples, a diode array detector, coupled with the UV-detector was used to obtain the UV-spectra of the detected compounds.

Table 5. Mean recovery rates, detection limits, determination limits and relative standard deviation of the method for the determination of triazine herbicides and its metabolites (determined by the method of the calibration curve)

Substance	Recovery rates [%]	Detection limit [ng/l]	Determination limit [ng/l]	Standard deviation of the method [%]
Hydroxysimazine	45.6			8.9
Desisopropylatrazine	30.9	18	27	3.8
Hydroxyatrazine	50.1			15.3
Desethylatrazine	89.7	20	31	4.4
Hydroxypropazine	42.5			21.7
Simazine	94.8	11	16	2.3
Cyanazine	96.3	16	25	3.5
Atratone	91.2	22	32	4.7
Desmetryne	95.0	19	28	4.0
Atrazine	91.2	16	24	3.5
Prometone	93.9	23	35	5.0
Methoprotryne	95.1	22	33	4.8
Terbumetone	92.8	45	67	10.1
Sebutylazine	96.0	27	40	5.8
Propazine	97.8	20	30	4.3
Terbutylazine	95.5	18	27	3.9
Prometryne	91.0	21	31	4.5
Terbutryne	89.4	22	33	4.8

Working range: 30 ng/l – 150 ng/l; n = 13

5.5 Reliability of the method

The detection limits and the determination limits were calculated according to the method of the calibration curve [9, 19].

They do not represent constant parameters but estimated values which depend on the number of the calibration concentrations, its distribution in the working range (equidistance), position and extent of the working range, the selected statistical certainty and the confidence interval of the calibration function (see Table 5).

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