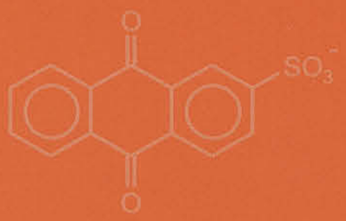
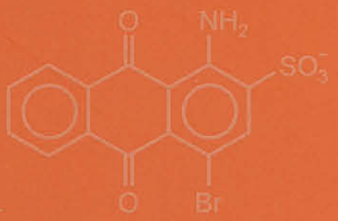
ASSOCIATION OF RIVER WATERWORKS

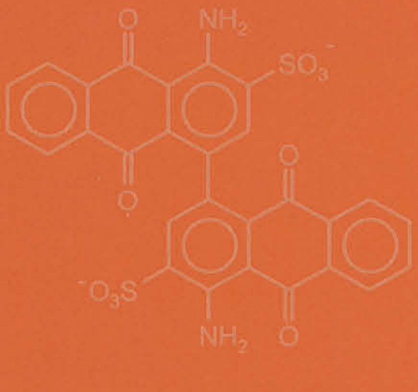
RIWA

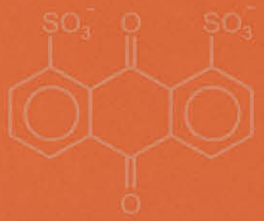
March 2000

Polar Aromatic Sulfonates and their Relevance to Waterworks









DVGW

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Polar Aromatic Sulfonates and their Relevance to Waterworks

Authors

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Publisher

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List of abbreviations:

1NS	1-naphthalenesulfonate
1,3NDS	1,3-naphthalenedisulfonate
1,5NDS	1,5-naphthalenedisulfonate
1,6NDS	1,6-naphthalenedisulfonate
1,7NDS	1,7-naphthalenedisulfonate
1,3,5NTS	1,3,5-naphthalenetrisulfonate
1,3,6NTS	1,3,6-naphthalenetrisulfonate
1O4NS	1-hydroxy-4-naphthalenesulfonate
2NS	2-naphthalenesulfonate
2,6NDS	2,6-naphthalenedisulfonate
2,7NDS	2,7-naphthalenedisulfonate
3ABS	3-aminobenzenesulfonate
3NBS	3-nitrobenzenesulfonate
3O2,7NDS	3-hydroxy-2,7-naphthalenedisulfonate
4O2,7NDS	4-hydroxy-2,7-naphthalenedisulfonate
6A2NS	6-amino-2-naphthalenesulfonate
6O4NS	6-hydroxy-4-naphthalenesulfonate
CAS	Chemical Abstracts Service
CTMA	cetyltrimethylammonium
GAC	granular activated carbon
LAS	linear alkylbenzenesulfonates
PAS	polar aromatic sulfonates
RPLC	reversed phase liquid chromatography
RP-SPE	reversed phase solid-phase extraction
SNFC	sulfonated naphthalene-formaldehyde condensates
SPE	solid-phase extraction
TBA	tetrabutylammonium

Summary

Scope of the survey

This literature survey comprises the present information on polar aromatic sulfonates (PAS) available from the English and German printed literature, from reports on existing chemicals, and from factual databases on hazardous substances. The search was restricted to those PAS which have been identified at least once in the aquatic environment.

One of the major concerns of this survey was to make the widespread information on PAS comparable. The search was complicated by the fact that for many of the relevant PAS there are a number of synonymes in use. Taking into account that up till now 37 PAS have been identified in the aquatic environment, the total of all known derivatives, e.g. free acids and the corresponding salts, would have been too high to be covered. For this reason mainly the technically important free acids, sodium or potassium salts are treated in this survey.

Production and uses of PAS

According to the *OECD List of High Production Volume Chemicals (1997)* 55 PAS or mixtures of PAS are produced or imported at volumes higher than 1,000 tons per year in at least one member country. 30 records contain PAS identified in the aquatic environment which equals a rate of identification of 55%.

The industrial production of PAS is based on the sulfonation of the appropriate aromatic hydrocarbons using sulfuric acid, oleum or sulfur trioxide. The sulfonation is frequently followed by a liming-out process to avoid desulfonation and isomerization. The amino derivatives are obtained from the original sulfonates by subsequent nitration and reduction, the hydroxy derivatives by caustic fusion.

Many PAS are used as precursors in the production of dyes, fluorescent whitening agents, synthetic tanning agents, dispersants, pharmaceuticals, and stabilizers. Another important field of application is the concrete industry. Especially the sulfonated naphthalene-formaldehyde condensates (SNFC) are important concrete plasticizers. Further applications of PAS are the use as textile auxiliaries, as additives for electroplating baths, and as acid catalyst.

Trace-analytical determination of PAS

Trace-analytical methods for PAS have been developed since about 1990 and there are protocols available for the selective and sensitive determination of PAS in the aquatic environment. However, standardized methods like for the pesticides do not yet exist and should be elaborated. The relevant methods of analysis are based on ion-pair reversed phase liquid chromatography, a special modification of high performance liquid chromatography (HPLC). Due to the low environmental PAS concentrations an extraction from the aqueous phase usually is neccessary. Solid-phase extraction by means of ion-pair extraction and extraction on an activated carbon material are adequate techniques for that purpose and have been applied to sewage, surface water and water after several steps of drinking water treatment.

Occurrence and behavior in the aquatic environment

In general, PAS are well water-soluble and have negative octanol/water partition coefficients. Consequently the accumulation in biota, sediments, and suspended solids is expected to be low. However, there is no systematic experimental investigation on sediments or other solid matrices.

PAS have been detected in landfill leachates, in sewages, in surface waters, and in bankside filtered waters. Up to now, there are no reports on investigations on their occurrence in groundwater.

PAS in landfill leachates were detected in a few waste dump sites in Switzerland and Germany. Concentrations of PAS up to 80 µg/L were ascribed to concrete admixtures resulting from construction waste and to the anaerobic cleavage of azo dyes. The identified benzene- and naphthalenesulfonates quite often are also found in sewages and surface waters.

26 PAS have been identified in sewages, though the number of publications on this topic is limited. In secondary effluents concentrations in the low mg/L range were reported for 2-amino-5-chloro-4-methylbenzenesulfonate, 1,5NDS, cis-4,4'-dinitro-2,2'-stilbenedisulfonate, and cis- and trans-4,4'-diamino-2,2'-stilbenedisulfonate. Many of the PAS identified in secondary effluents have also been detected in river water.

All measurements of PAS in surface waters are referring to river and creek waters. No lakes have been investigated. Monitoring programmes have been carried out at the Rhine, Elbe, and Danube rivers. The most widespread occurring PAS are the naphthalenesulfonates. They seem to be ubiquitarily distributed in anthropogenically influenced rivers. Typical concentrations are in the range from 10 ng/L to 10 µg/L. In the Elbe river concentrations up to 100 µg/l are observed. The highest concentrations occurring in river water were reported from the small Italian Bormida river. However, a large percentage of waste water has to be assumed for this river. Higher concentrations of single PAS are only observed when PAS producing or consuming companies are situated in the drainage area of the correponding streams.

The occurrence of certain PAS in secondary effluents and the corresponding water bodies demonstrates their recalcitrant properties. However, based on the present literature on the degradation of PAS by bacteria and microalgae, the general opinion that all or most aromatic sulfonates are not or not readily biodegradable is not true. The observed biodegradabilities depend strongly on the test conditions and range from readily degradable to non-degradable. There are large differences in the biodegradability of individual PAS. Correlations with their molecular structure are recognizeable. In general multiple sulfonated compounds and compounds with additional substituents are less readily degraded than monosulfonated PAS. Furthermore, there are also drastic changes in the biodegradability between isomers, e.g. for the different naphthalenedisulfonates. Surprisingly, the qualitative results of typical waste water tests correspond quite well with the findings of field studies in sewage treatment plants and during bankside filtration.

For the elimination of PAS from the raw waters of the water works a multibarrier approach is needed in order to remove PAS traces of about 1 µg/L down to concentrations below the analytical detection limits, which are of the order 0.1 µg/L. Only oxidation by ozone is not effective enough. A combination of ozone treatment with an adsorption step using frequently reactivated/exchanged activated charcoal is suited for that purpose.

From the multitude of PAS a few compounds seem to be relevant to drinking water. Only naphthalenesulfonates, mainly di- and trisulfonates, have been identified in drinking water. However, there are only little data published on drinking water investigations. 1,5NDS and 1,3,6NTS have to be mentioned as relevant to drinking water. Extension of measurements of PAS in drinking water is recommended.

Toxicity and ecotoxicity

Toxicity and ecotoxicity data sets are incomplete for many PAS, very likely due to their use as intermediates or due to their occurrence as by-products in technical mixtures. Concerning acute toxicity, it is ordinarily supposed that PAS are less toxic than the corresponding non-sulfonated compounds. In general the introduction of sulfo groups causes a strong detoxification even of highly toxic substances. The known LD50 values for acute toxicity are of the order of g/kg and, therefore, far above the uptake from water which is contaminated with PAS on the µg/L level. However, due to the lack of chronic toxicity data, it is not possible to assess risks due to long term exposition of organisms to the PAS traces found in surface waters and drinking water. Therefore, PAS immissions in raw waters should be reduced and further testings on risks of long term exposition are recommended.

1 Introduction

1.1 Background

Aromatic sulfonates belong to the oldest organic chemicals which have been produced since the end of the last century on an industrial scale, especially in the synthesis of dyestuffs and in general as versatile intermediates in the synthesis of organic compounds. Over the decades new fields of application of sulfonated aromatic compounds have been discovered, e.g., their use as tensides or fluorescent whitening agents in laundry products, as dispersing agents in manifold industrial processes, as concrete plasticizers and synthetic tanning agents.

For more than 20 years residues of these well water-soluble anthropogenic compounds have been expected in natural waters. Except for sulfonated active agents of washing and cleaning products until the 1990s there was a lack of measured concentrations for individual aromatic sulfonates in the aquatic environment.

After the development of new trace-analytical methods about ten years ago, a number of sulfonates have been identified and quantified in natural waters of several European countries, mainly in Germany, Switzerland, Italy, Hungary and The Netherlands. Nowadays, several work groups deal with the analytical determination of these compounds and year by year the knowledge on sources and occurrence in the aquatic environment becomes more evident.

Due to the high water solubility and in certain cases poor biodegradability, which is ascribed to aromatic sulfonates, measurable quantities were expected in the wells of water works, especially if bankside filtration of river water is applied. Meanwhile, this assumption was proved, and there are first reports on the occurrence of aromatic sulfonates even in drinking water.

However, although the number of aromatic sulfonates identified in the aquatic environment is continuously growing, there is still no comprehensive review on the widespread information available, and therefore, no basis for a first assessment of possible risks.

With this background it seemed to be worth-wile to create a sound platform for water companies, which might be confronted with the topic of sulfonate traces in their water.

In this literature survey the present data about aromatic sulfonates in the aquatic environment were compiled and evaluated.

1.2 Scope of the study

Besides alkyl-, hydroxy-, amino-, nitro- and halogen groups the sulfo group is one of the most frequently occurring groups in synthetic organic compounds. There are thousands of aromatic and aliphatic compounds with at least one sulfo group in their molecule, which all could be called sulfonic acids and their salts sulfonates. However, only a limited number of these compounds have to be taken into account from the viewpoint of water and especially drinking water contamination. There are four main criteria which determine, whether a compound is relevant to water works or even to drinking water, i.e.,

- toxicity,
- production and consumption volumes,
- aqueous solubility, and
- persistency against any kind of degradation.

Toxicity is the most important of these criteria. Acute and chronic toxicity both have to be taken into account. Effect levels of acute toxicities for many trace chemicals in the aquatic environment are orders of magnitude higher than the observed concentrations. For the assessment of toxic effects caused by environmental chemicals it is also important to have information on the chronic affects generated by long term exposition of these chemicals to certain organisms.

Only those sulfonates can be expected to occur in measurable quantities in the environment which are produced or used in sufficiently large amounts, so that traces of them will still remain after dilution and degradation processes.

On the basis of aqueous solubility the huge number of sulfonated organic compounds can roughly be classified into polar and non-polar sulfonates although the transition is fluent. The physicochemical properties of the latter ones are determined by a large non-polar structural unit, whereas the properties of polar sulfonates are dominated by the sulfo group(s), and therefore, resemble very much the properties of inorganic anions. The fluorescent whitening agents are a typical example of non-polar sulfonates. These chemicals, which are relevant, e.g., for sediment pollution of lakes, are not very interesting for water works due to their comparatively high octanol/water partition coefficient (hydrophobic compounds) and, therefore, the concentrations in water itself are expected to be low.

The fourth criterion, the biodegradability, also excludes a number of easily degradable compounds from further considerations with respect to their relevance to water works. As a prominent example, the class of the linear alkylbenzenesulfonates (LAS) is easily degraded in sewage treatment plants, and therefore, should not constitute a problem to the drinking water treatment in industrialized countries. However, the LAS metabolites, the sulfophenyl-carboxylates (SPC) are even more polar than the parent compounds and their relevance to the environment is a matter of current research.

Based on these considerations only small polar aromatic sulfonates[1] or highly sulfonated compounds, which derive from benzene, naphthalene, anthraquinone and stilbene,

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[1] In the following the abbreviation **PAS** is used for small polar aromatic sulfonates.

will be discussed in this survey. Moreover, this study comprises only those PAS, which were identified at least once in the aquatic environment.

The survey starts with an overview of the properties and structures of the relevant PAS. Subsequently, the production and uses of technically important PAS are given in order to show known and potential sources of these compounds. In the following the existing trace-analytical methods for the determination of PAS in water samples are described. A summary of the data on the occurrence of PAS in natural waters is following. The final chapter deals with different aspects of PAS during the drinking water treatment.

2 Structures and properties of polar aromatic sulfonates

2.1 Search strategy for the compilation of physicochemical, toxicological and ecotoxicological properties, and of biodegradability data

In order to get a comprehensive overview on the properties of PAS relevant to aqueous systems, different databases and reports on existing chemicals were studied in addition to the literature cited in the reference list.

RTECS database: ”Registry of Toxic Effects of Chemical Substances” by the U.S. Secretary of Commerce on Behalf of the U.S. Government. This National Institute of Occupational Safety and Health (NIOSH) file is a compendium of toxicity data extracted from the scientific literature. The information is available on the INTERNET via STN International (http://www.fiz-karlsruhe.de/stn.html).

ECDIN databank: The ”Environmental Chemicals Data and Information Network” is a factual databank created under the Environmental Research Programme of the European Commission, Joint Research Centre at the Ispra Site, Italy. The ECDIN databank has recently been updated by PHATOX - Pharmacological and Toxicological Data and Information Network. This information is available on the INTERNET (http://ecdin.etomep.net/Ecdin/E_hinfo.html).

HSDB: The ”Hazardous Substances Data Bank” (HSDB), is a factual, non-bibliographic database from the Toxicology Program of the National Library of Medicine. It contains information on toxicology and environmental effects of chemicals.

AIDA database: The ”Altstoff-Informationsdatenbank” (AIDA) is a database on existing chemicals published by the VCI (Verband der Chemischen Industrie), the association of the German chemical industry. It contains basic data sets including physicochemical, ecotoxicological and toxicological data, and information on regulations and exposition.

BUA reports: The Advisory Committee on Existing Chemicals of Environmental Relevance (BUA) of the German Chemical Society (GDCh) systematically evaluates existing chemicals. The results of these evaluations are published as reports on single chemicals and chemical groups.

CS ChemFinder: The CS ChemFinder WebServer (http://chemfinder.camsoft.com/) is an INTERNET index specifically tailored to store and present information about individual chemical substances. This search engine has been designed to meet the specific challenges of finding chemical information.

Considering the large number of compounds and the complexity of their systematic names it was essentially to obtain the Chemical Abstract Service (CAS) registry numbers. Those registry numbers are convenient entries when large databases are searched and errors are less likely to occur, compared to entering names. Information on the substance ”4-

methylbenzenesulfonate" (IUPAC name) for example is available under the following chemical and commercial names:

p-toluenesulfonic acid, sodium salt,
benzenesulfonic acid, 4-methyl-, sodium salt (9CI),
Naxonate hydrotrope; sodium,
p-methylbenzenesulfonate; sodium,
sodium paratoluene sulphonate,
sodium p-toluenesulfonate,
sodium p-tolyl sulfonate,
sodium tosylate,
4-toluenesulfonic acid, sodium salt

Furthermore, the spelling of "sulfonate" is not uniform; sometimes it is written with "ph". However, even the knowledge of CAS registry numbers may also not be sufficient, because the sulfonates differ in the corresponding cations. If toxicological or irritation tests are carried out with free acids (free sulfonic acids are strong acids) or the sodium/potassium salts, this may be substantial. In Table 2-1 the IUPAC names of the sulfonic acids relevant for aqueous systems are given together with their CAS registry numbers and the corresponding cations. In five cases no CAS registry numbers could be found.

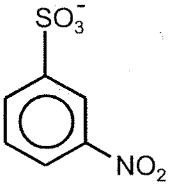
Table 2-1: Free acids, sodium and potassium salts of polar aromatic sulfonates relevant to the aquatic environment; the number of crosses (x) in columns 3 to 5 indicate the number of free sulfonic acid groups (H^+) and of sodium (Na^+) and potassium ions (K^+) per sulfonate molecule.

compound (IUPAC name)	**CAS registry number**	**H^+**	**Na^+**	**K^+**
benzenesulfonates				
3-nitrobenzenesulfonate	127-68-4		x	
4-nitrobenzenesulfonate	138-42-1	x		
3-aminobenzenesulfonate	1126-34-7		x	
4-aminobenzenesulfonate	121-57-3	x		
4-hydroxybenzenesulfonate	1333-39-7	x		
4-methylbenzenesulfonate	657-84-1		x	
	104-15-4	x		
5-nitro-2-methylbenzenesulfonate	121-03-9			
3-chloro-4-methylbenzenesulfonate	5138-91-0		x	
2-amino-5-chloro-4-methylbenzenesulfonate	88-53-9	x		
4-(1-methylethyl)benzenesulfonate	28348-53-0	x		
2-amino-1,4-benzenedisulfonate	98-44-2	x		
naphthalenesulfonates	68155-01-5			
1-naphthalenesulfonate (1NS)	130-14-3		x	
	85-47-2	x		
2-naphthalenesulfonate (2NS)	532-02-5		x	
1,3-naphthalenedisulfonate (1,3NDS)	-			
1,5-naphthalenedisulfonate (1,5NDS)	1655-29-4		xx	
1,6-naphthalenedisulfonate (1,6NDS)	1655-43-2		xx	
1,7-naphthalenedisulfonate (1,7NDS)	5724-16-3			
2,6-naphthalenedisulfonate (2,6NDS)	1655-45-4			
2,7-naphthalenedisulfonate (2,7NDS)	1655-35-2		xx	
1,3,5-naphthalenetrisulfonate (1,3,5NTS)	6654-64-4			

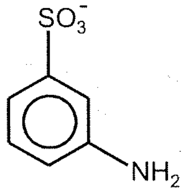
compound (IUPAC name)	CAS registry number	H$^+$	Na$^+$	K$^+$
1,3,6-naphthalenetrisulfonate (1,3,6NTS)	5182-30-9		xxx	
methylenebis-2-naphthalenesulfonate (5,5'-, 8,8'- and 5,8'-isomers)	-			xx
2-amino-1,5-naphthalenedisulfonate	117-62-4	x		
3-amino-1,5-naphthalenedisulfonate	131-27-1			
7-amino-1,3-naphthalenedisulfonate	86-65-7	xx		
	842-15-9	x	x	
3-hydroxy-2,7-naphthalenedisulfonate	135-51-3		xx	
4-hydroxy-2,7-naphthalenedisulfonate	20349-39-7		xx	
7-hydroxy-1,3-naphthalenedisulfonate	118-32-1			
anthraquinonesulfonates				
2-anthraquinonesulfonate	131-08-8		x	
1-amino-4-bromo-2-anthraquinonesulfonate	116-81-4	x		
1,8-anthraquinonedisulfonate	-			
4,4'-diamino-1,1'-bianthraquinone-3,3'-disulfonate	-			
stilbenesulfonates				
4,4'-diamino-2,2'-stilbenedisulfonate	7336-20-1		xx	
	81-11-8	xx		
4,4'-dinitro-2,2'-stilbenedisulfonate	3709-43-1			
other sulfonates				
2-Hydroxy-4,6-bis(4-sulfanilo)-1,3,5-triazine	-			

2.2 Molecular structures of polar aromatic sulfonates

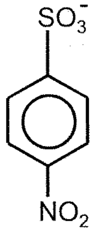
In order to better visualize the subject of this study, in the following figures 2-1a – 2-1d the molecular structures of the PAS discussed in this study are shown.



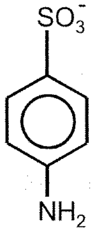
3-nitrobenzenesulfonate



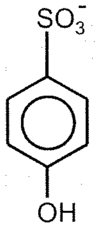
3-aminobenzenesulfonate



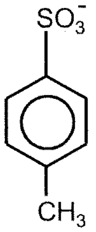
4-nitrobenzenesulfonate



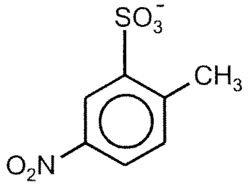
4-aminobenzenesulfonate



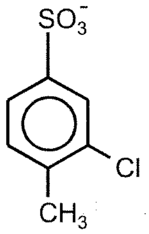
4-hydroxybenzenesulfonate



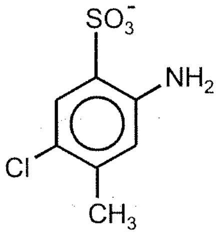
4-methylbenzenesulfonate



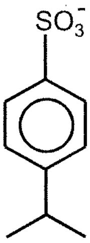
5-nitro-2-methylbenzenesulfonate



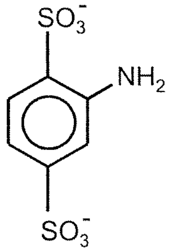
3-chloro-4-methylbenzenesulfonate



2-amino-5-chloro-4-methylbenzenesulfonate

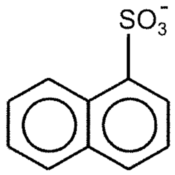


4-methylethyl-benzenesulfonate

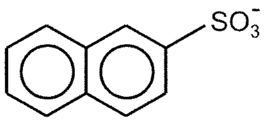


2-amino-1,4-benzenedisulfonate

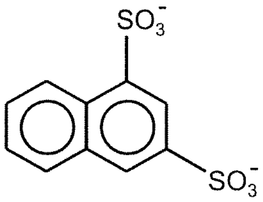
Figure 2-1a: Benzenesulfonates identified in the aquatic environment



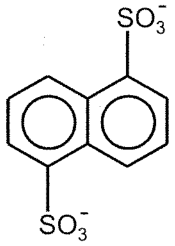
1-naphthalenesulfonate



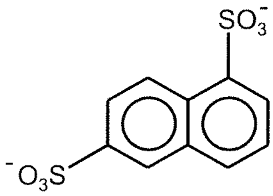
2-naphthalenesulfonate



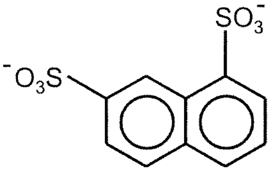
1,3-naphthalenedisulfonate



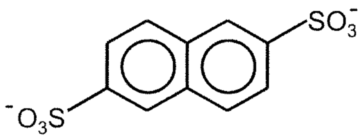
1,5-naphthalenedisulfonate



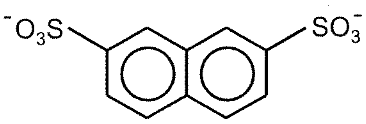
1,6-naphthalenedisulfonate



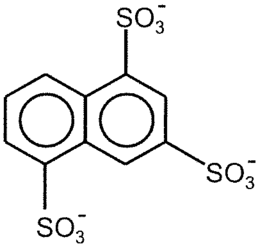
1,7-naphthalenedisulfonate



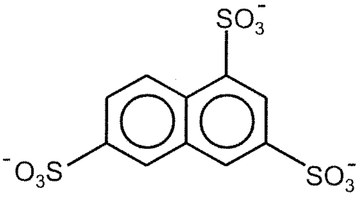
2,6-naphthalenedisulfonate



2,7-naphthalenedisulfonate

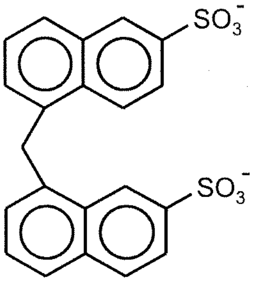


1,3,5-naphthalenetrisulfonate

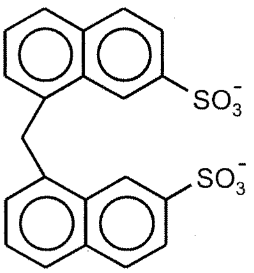


1,3,6-naphthalenetrisulfonate

Figure 2-1b: Naphthalenemono-, -di-, and -trisulfonates identified in the aquatic environment



5,8'-methylenebis-2-naphthalenesulfonate



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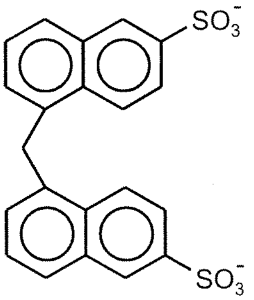
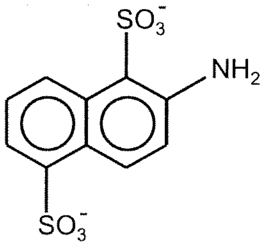
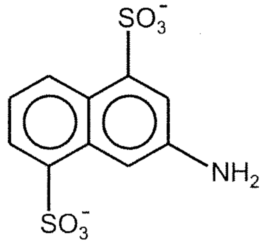


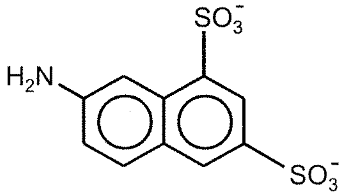
5,5'-methylenebis-2-naphthalenesulfonate



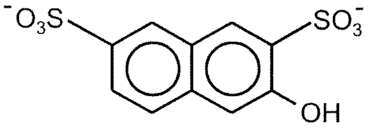
2-amino-1,5-naphthalenedisulfonate



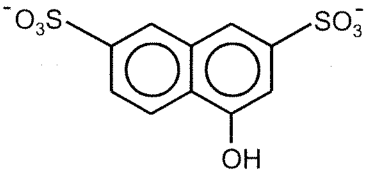
3-amino-1,5-naphthalenedisulfonate



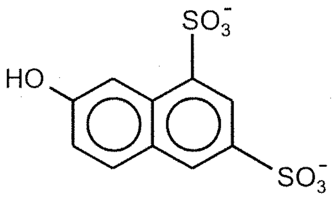
7-amino-1,3-naphthalenedisulfonate



3-hydroxy-2,7-naphthalenedisulfonate

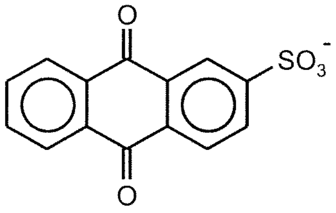


4-hydroxy-2,7-naphthalenedisulfonate

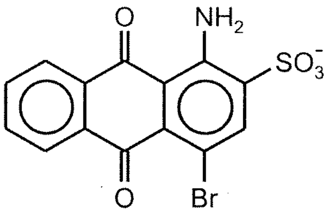


7-hydroxy-1,3-naphthalenedisulfonate

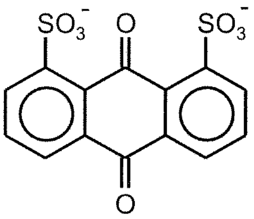
Figure 2-1c: 2:1-condensates of 2NS with formaldehyde, amino- and hydroxynaphthalenesulfonates identified in the aquatic environment



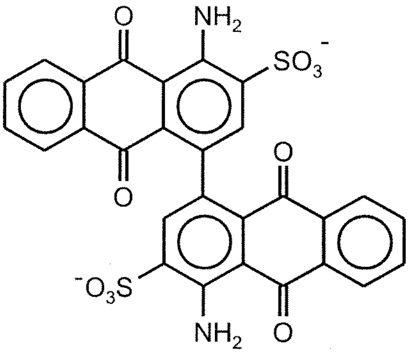
2-anthraquinonesulfonate



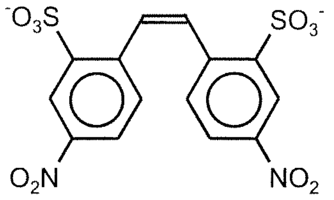
1-amino-4-bromo-2-anthraquinonesulfonate



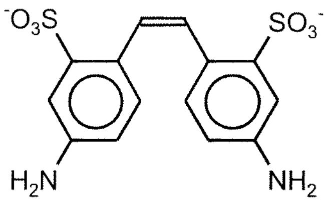
1,8-anthraquinonedisulfonate



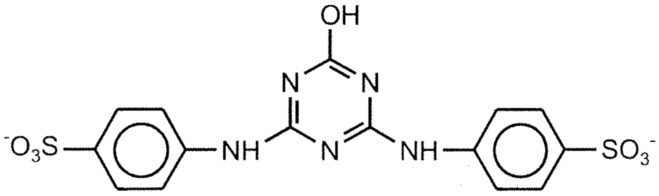
4,4'-diamino-1,1'-bianthraquinone-3,3'-disulfonate



4,4'-dinitro-2,2'-stilbenedisulfonate



4,4'-diamino-2,2'-stilbenedisulfonate



2-hydroxy-4,6-bis(4-sulfanilo)-1,3,5-triazine

Figure 2-1d: Anthraquinonesulfonates, stilbenesulfonates, and a sulfonated hydroxytriazine identified in the aquatic environment

2.3 Physicochemical data

In this subchapter the octanol/water partition coefficients and aqueous solubilities are of special interest, because they are a measure for affinity of chemicals against the aqueous phase and biota or sediments/suspended solids, respectively. High aqueous solubilities and negative log K_{OW} values indicate that a certain substance is likely to be dissolved in the aqueous phase, although there are exceptions. For example, ionic interactions between the chemical and soil, which lead to adsorption of the compound, can occur. This is primarily the case, if the considered substance has a positive charge, and therefore is able to interact with the negative surface charges of soil particles. But in general, bioaccumulation and adsorption to sediments and suspended solids are not expected to play an important role for substances with high aqueous solubilities and negative log K_{OW} values. On the other hand, this means that these substances are likely to be found in the raw waters of the water works.

Table 2-2 shows the octanol/water partition coefficients and aqueous solubilites of some PAS. Though these data are scarcely available, the properties of these substances can easily be estimated. Caused by the ionic and polar structure the water solubility should be high and consequently the transfer into the octanol phase low.

Table 2-2: Octanol/water partition coefficients and aqueous solubilities of PAS

compound (IUPAC name)	log K_{OW} (sodium salt)	aqueous solubility (sodium salt)
benzenesulfonates		
3-nitrobenzenesulfonate	-2.6 (OECD test, guideline 107)	336 g/L (25 °C)
3-aminobenzenesulfonate	-3.4	
4-aminobenzenesulfonate	-2.16	< 1 g/L (20°C, free acid)
4-methylbenzenesulfonate		"very soluble in water"
3-chloro-4-methylbenzenesulfonate		"very soluble in water"
naphthalenesulfonates		
1-naphthalenesulfonate		91 g/L (10 °C)
		77 g/L (10 °C)
2-naphthalenesulfonate		59 g/L (25 °C)
		67 g/L (10 °C)
1,5-naphthalenedisulfonate	-0.4 (free acid; calculation[1)])	111 g/L (18 °C)
		67 g/L (18 °C)
1,6-naphthalenedisulfonate		333 g/L (18 °C)
		200 g/L (18 °C)

compound (IUPAC name)	log K_{OW} (sodium salt)	aqueous solubility (sodium salt)	
2,6-naphthalenedisulfonate		119 g/L	(18 °C)
		52 g/L	(18 °C)
2,7-naphthalenedisulfonate		450 g/L	(18 °C)
		710 g/L	(10 °C)
anthraquinonesulfonates			
1-amino-4-bromo-2-anthraquinoesulfonate	1,2 (free acid, calculation[1)])	20 g/L	(15 °C)
stilbenesulfonates			
4,4'-diamino-2,2'-stilbenedisulfonate	-1.7 (free acid; calculation[1)])	> 100 g/L	(19°C)
		0.65 g/L	(free acid)

1) calculation: according to Leo and Hansch

2) If not indicated otherwise, the data are from the reports/factual databases given in 2.1.

2.4 Toxicity data

PAS are supposed to be less toxic than the corresponding non-sulfonated compounds. The sulfo group is in general strongly detoxifying. Even highly toxic compounds, such as aniline, 2-naphthylamine, or various nitroaromatics, become nontoxic when sulfonic acid groups are introduced [1]. The addition of the sulfonic acid group usually changes a lipophilic compound, which easily penetrates the skin, to a hydrophilic one, which will hardly penetrate the skin. After oral uptake they are expected to be rapidly excreted in the urine either as such, or as a conjugate with glycine of glucuronic acid.

The acute toxicities of the non-sulfonated parent compounds when considering oral uptake often are of the same order of magnitude as for PAS, i.e. in the g/kg range. However, the long term exposition of the non-sulfonated chemicals (e.g. benzene, aniline, phenol) in many cases leads to severe health damages to humans. Data on toxicological effects of PAS to humans have not been found in this research.

The above remarks apply to the sulfonic acids and their common salts. Other derivatives may be more toxic. For example, 4-methylbenzenesulfonic acid is only a skin irritant, but its sulfonyl chloride and its methyl ester are both potent vesicants. However, harmful substances may be still be formed from harmless substances, for example, in waste water treatment plants or other natural reactors.

In this study we were searching for data on acute toxicity, irritation, repeated dose toxicity, genotoxicity, carcinogenicity and reproductive effects. Only for 11 PAS of 37 in total relevant for the aquatic environment acute toxicity or irritation data were available. Most of the acute toxicity tests were carried out with rats and mice (sometimes also with guinea pigs).

Oral dosage was most often applied, sometimes inhalation, intravenous and intraperitoneal applications were given. LD50 values obtained after oral dosage range from 2 to 50 g/kg. The results of the irritation tests vary from "non-irritating" (3-nitrobenzenesulfonate: eyes, rabbit) to severe effects. Maybe strongly irritating effects would be obtained if the experiments were carried out with the free acids. However, this was not always clearly documented in the databases. Table 2-3 gives a summary of acute toxicity and irritation data.

Data on repeated dose toxicity (2 entries), genotoxicity (4 entries), carcinogenicity (1 entry) and reproductive effects (1 entry) could rarely be found. Obviously, these tests have not yet been carried out because PAS are generally thought to be of minor toxicological relevance. In the case of repeated oral dosage of 3-nitrobenzenesulfonate to cats (2 and 4 g/kg) trembling and vomiting was observed. Genotoxicity data were found for 3-nitrobenzenesulfonate, 3-aminobenzenesulfonate, 4-aminobenzenesulfonate, 1,5-naphthalenedisulfonate and 4,4'-diamino-2,2'-stilbenedisulfonate. All results obtained by the Ames test were negative.

Table 2-3: Summary of acute toxicity and irritation data of PAS

	acute toxicity	**irritation**
benzenesulfonates		
3-nitrobenzenesulfonate	species: rat; dosage: oral LD50: > 5 (11) g/kg species: mouse; dosage: oral LD50: > 3.2 g/kg species: rat; dosage: inhalation LD50: > 5.1 mg/L/4h species: rat; dosage: inhalation no mortality after 7h species: mouse; dosage: i.p. LD50: 2,3 g/kg	species: rabbit (Draize test) skin: non irritating eye: non irritating
3-aminobenzenesulfonate	species: rat LD50: 5.2 g/kg	eye: strongly irritating skin: no data
4-aminobenzenesulfonate	species: rat; dosage: oral LD50: 12 g/kg dosage: intravenous LD50: 6 g/kg	eye: moderately irritating skin: slightly irritating
4-hydroxybenzenesulfonate	species: mouse dosage: intravenous LD50: 1.7 g/kg	-
5-nitro-2-methylbenzenesulfonate	species: rat dosage: oral LD50: 3.7 g/kg	species: rabbit route: skin, dose: 20 mg, duration: 24 h, effect: moderate; route: eyes, dose: 2 mg, duration: 24 h, effect: severe
2-aminobenzene-1,4-disulfonate	-	species: rabbit route: skin, dose: 500 mg, duration: 24 h, effect: mild; route: eyes, dose: 100 mg, duration: 24 h, effect: moderate

	acute toxicity	irritation
naphthalenesulfonates		
2-naphthalenesulfonate	species: rat; dosage: oral LD50: 14 g/kg	-
1,5-naphthalenedisulfonate	species: rat dosage: oral LD50: > 2 g/kg	species: rabbit route: ear; dose: 500 mg free acid; duration:24h, semi-occlusive, (observation time 7 h), strongly irritating; OECD guideline No. 404 skin: non irritating; OECD guideline 405 eye: non irritating; dosage: 50 mg (free acid) observation time 7 h eye: strongly irritating
2-amino-1,5-naphthalenedisulfonate	species: rat route: oral LD50: 5.4 g/kg	species: rabbit dosage: skin; dose: 500 mg, duration 24 h, effect: mild dosage: eyes, dose: 20 mg duration 24 h, effect: moderate
anthraquinonesulfonates		
2-anthraquinonesulfonate	species: rat dosage: oral, LD > 8 g/kg dosage: intraperitoneal LD50: 0.73 g/kg; species: mouse dosage: oral, LD > 8 g/kg dosage: intraperitoneal LD50: 0.63 g/kg; species: guinea pig dosage: oral, LD50 21 g/kg	-
1-amino-4-bromo-2-anthraquinonesulfonate	species: rat dosage: oral, LD > 5 g/kg (> 20 g/kg, second source)	species: rabbit route: ear, dose: 500 mg, (duration 24 h, semi occlusive observation 7 d) route: skin, eyes dose: - not irritating
stilbenesulfonates		
4,4'-diamino-2,2'-stilbenedisulfonate	species: rat dosage: oral, > 5 g/kg no symptoms (di-sodium-salt); species: guinea pig dosage: oral, LD50: 47 g/kg	species: rabbit route: ear, dose: 500 mg, duration 24 h, semi occlusive (observation 7 d, di-sodium-salt); species: rabbit dose: 50 mg, observation time 7 d, slightly irritating, (di-sodium-salt)

2.5 Ecotoxicity data

Ecotoxicological data were only available in the case of three benzenesulfonates (3-nitro-, 3-amino-, and 4-amino-), 1,5-naphthalenedisulfonate and 4,4'-diamino-2,2'-stilbenedisulfonate. The results are shown in table 2-4. The ecotoxicological tests show that effects will only be detectable, if the concentrations of PAS are higher than 0.1 g/L. At present there are no legally binding requirements or quality targets for these compounds.

Table 2-4: Results of ecotoxicity tests on fish, small crustaceans, algae and bacteria

	fish (Leuciscus idus)	**small crustaceans** (daphnia magna)	**algae**	**bacteria**
benzenesulfonates				
3-nitrobenzene-sulfonate	exposure: 48 h LC50: > 500 mg/L	exposure: 48 h LC50: 9 g/L; exposure: 4 d TGK: 230 mg/L	-	exposure: 17 h EC10: >10 g/L EC50: >10 g/L EC90: >10 g/L; (pseudomonas putida, DIN 38412) - EC20: > 2 g/L (activated sludge)
3-aminobenzene-sulfonate	exposure: 96 h LD50: > 10 g/L	exposure: 24/48 h EC50: > 500 mg/L	exposure: 72 h EC20: 140 mg/L exposure: 96 h EC20: 470 mg/L exposure: 72/96 h EC50: > 500 mg/L exposure: 71/96 h EC90: 500 mg/L	exposure: 17 h EC50: 7 g/L
4-aminobenzene-sulfonate	exposure: 48 h LD0: > 1 g/L; exposure: 96 h LC50: 100 mg/L	exposure: 24 h EC50: 100 mg/L	-	exposure: 24 h EC0: 10 g/L
naphthalenesulfonates				
1,5-naphthalene-disulfonate	exposure: 96 h LC0: 10 g/L	-	-	
anthraquinonesulfonates				
1-amino-4-bromo-2-anthraquinone-sulfonate	exposure: 48 h LC0: 0.1 g/L LC100: 0.2 g/L	-	-	exposure: 24 h EC0: 10 g/L (Pseudomonas fluorescens, DEV, L8)
4,4'-diamino-2,2'-stilbenedisulfonate	exposure: 48 h LC0: 200 mg/L	-	-	exposure: 24 h EC0: 1 g/L (pseudomonas fluorescens, DEV, L8)

2.6 Biodegradability data

2.6.1 General aspects of the biodegradability of sulfonated aromatic compounds

Biodegradation of organic micropollutants is an important compound property with respect to elimination processes, both in sewage treatment plants and in the water purification process in water works. The elimination of PAS in sewage treatment plants is treated in *subchapter 5.2* "Occurrence of polar aromatic sulfonates in sewage". In the following, results of laboratory degradation experiments with selected PAS are given.

The initial reaction of the biodegradation of benzene or naphthalene compounds by bacteria under aerobic conditions is catalyzed by dioxygenases. Like halogen- or nitro-substituents also the sulfo-group hinders the electrophilic attack of the arene dioxygenases. This effect is discussed in the literature in terms of steric hindrance, the electron withdrawing by the sulfo group and by the difficulty of an active transport of the charged sulfonate ions into the cells.

2.6.2 Benzenesulfonates

Amino- and nitrobenzenesulfonates

The degradation of the technically important nitro- and aminobenzenesulfonates was studied by several authors. A survey of the relevant literature until 1993 is given in the introduction of an article of Kölbener et al. [2]:

The biodegradation of aromatic compounds containing sulfo- and nitro-substituents, or sulfo- and amino-substituents, especially when these are in the 1,3-position, is considered to be problematic [3], and conflicting reports on the biodegradability of 3NBS and 3ABS occur in the literature. Zürrer et al. [4] showed conclusively that Pseudomonas putida S313 can quantitatively desulfonate 3NBS and 2ABS in the absence of sulfate. Locher et al. [5] obtained pure cultures which could quantitatively utilize either 3NBS or 3ABS as a sole source of carbon and energy for growth, and one of these organisms was used to degrade 3ABS in model wastes [6]. The observed degradation rates were low and these organisms were not salt tolerant. 2NBS was not degraded by these organisms. However, no significant elimination or mineralization of 3ABS has been detected in at least six different OECD tests [3,7], though Gerike [8] detected partial (18%) elimination of this compound in the test for recalcitrant metabolites. Similarly, Baumann et al. [9] detected no degradation of 3NBS with either the OECD-test 302B or a trickling filter. In contrast, partial degradation of 3NBS (62% [10]) and extensive elimination of 3NBS (>90%; OECD test 302B) have been reported [11].

The investigation of Kölbener et al. [2] on the degradability of 3NBS and 3ABS in a laboratory trickling filter gave the following results. No activated sludge from four municipal treatment plants could degrade 3NBS or 3ABS. In contrast, each of the sludges from two plants treating sewages from the textile industry was able to completely degrade 3NBS or 3ABS. Under certain conditions, municipal activated sludge could acclimate to degrade 3NBS, even though inoculation with a degradative sludge was a more efficient process. In the absence of a carbon source, the degradative ability of trickling filters was retained for at least one week; thereafter, an adaptation phase was required before rapid and extensive degradation of 3NBS recovered. The global parameters DOC and release of CO_2 indicated incomplete metabolism of 3NBS, but this effect was found to be due to the presence of a non-degraded impurity (5%), 4NBS, found in most commercial preparations of 3NBS.

In the context of his studies on textile sewage treatment Altenbach [12] also carried out aerobic degradation tests according to OECD 302 B and by shaking test solutions of benzene- and naphthalenesulfonates in Erlenmeyer flasks. The initial concentration of the test compounds were between 35 and 50 mg/L, calculated as DOC. Using activated sludge which was acclimated to textile sewage he found a ready degradation of 3- and 4NBS with single component solutions and also with isomer mixtures. After 10 days at 25°C the degradation was nearly complete. 2NBS was not degraded within 28 days. By following the DOC decrease, there was no evidence for any stable metabolites. At 10°C the experiments showed only a small decrease in 3- and 4NBS concentrations over 28 days.

Using activated sludge from a municipal sewage treatment plant, a slow almost continuous elimination of both, 3NBS and 4NBS, was observed. About 10 and 25% of 3NBS and 4NBS, respectively, remained in the test solution after 28 days. The finding that 4NBS was readily degraded in the laboratory experiment with acclimated activated sludge was different to the finding of Kölbener et al. [2], who found 4NBS to be non-degradable with sludge from the same sewage treatment plant.

4-Methylbenzenesulfonate (p-toluenesulfonate)

There is a number of papers on the biodegradation of 4-methylbenzenesulfonate. In the single compound BUA report [13] on this substance an extensive review is given, and therefore, this item should not be discussed in detail here. Most of the authors cited in this review found 4-methylbenzenesulfonate to be readily biodegradable under aerobic conditions, either by pure microorganism cultures or by mixed cultures.

2.6.3 Naphthalenenesulfonates

The biodegradation of naphthalenesulfonates was extensively studied by the researchers around Knackmuss [14-18]. These authors isolated several bacterial strains from sewage and surface water, which are able to degrade different naphthalenesulfonates either as pure cultures or in mixed cultures.

Brilon et al. [14,15] were the first who obtained naphthalenesulfonic acid-utilizing bacteria by continuous enrichment from a naphthalene-degrading population from sewage. In addition to naphthalene, Pseudomonas sp. A3 can utilize 2NS and Pseudomonas sp. C22 can utilize both 1NS and 2NS as sole carbon sources. In a mixture of 1NS and 2NS, the former substrate is utilized by strain C22 only after complete consumption of 2NS. During exponential growth, approximately 10% of the organic carbon of naphthalenesulfonates is temporarily excreted. These unidentified metabolites can readily be used by other bacteria, which, by supplying strain C22 with vitamins, allow optimal growth in stable mixed cultures. The degradative capability of Pseudomonas sp. A3 for 2NS was irreversibly lost under nonselective growth conditions and could be transferred from the wild type to a distinguishable cured strain of the wild type. For 2NS these authors showed that dioxygenation in 1,2-position weakens the C-S bond and the hypothetical intermediate, i.e. 1,2-dihydroxy-1,2-dihydro-2-naphthalenesulfonate eliminates the sulfo group as sulfite. The resulting rearomatization product, 1,2-dihydroxynaphthalene is a metabolite of the usual naphthalene degradation path. In contrast to the classical naphthalene utilizing bacteria the naphthalenesulfonate degrading bacteria convert salicylic acid by means of a salicylic acid-5-hydroxylase via the gentisic acid pathway [17].

Nörtemann et al. [16] isolated a 6-amino-2-naphthalenesulfonate(6A2NS)-degrading mixed bacterial community from a sample of river Elbe water. The complete degradation of this compound may be described by a mutual interaction of two Pseudomonas strains isolated from this culture. One strain, BN6, could also grow on 6A2NS in monoculture, however, with accumulation of black polymers. This organism effected the initial conversion of 6A2NS into 5-aminosalicylate through regioselective attack of the naphthalene skeleton in the 1,2-position. 5-aminosalicylate was totally degraded by another member of the community, strain BN9. After prolonged adaptation of strain BN6 to growth on 6A2NS, this organism readily converted all 2-naphthalenesulfonates with OH- or NH_2-substituents in the 5-, 6-, 7-, or 8-position. The corresponding hydroxy- or aminosalicylates were excreted in stoichiometric amounts, with the exception that the metabolite from 5A2NS oxidation was not identical with 6-aminosalicylate.

Wittich et al. [18] isolated a 2,6NDS-degrading Moraxella strain from an industrial sewage. This culture could also be adapted to 1,6NDS as growth substrate. Regioselective 1,2-dioxygenation effected desulfonation and catabolism to 5-sulfosalicilate, which also could be used as sole carbon source. 5-sulfosalicilate-grown cells exhibit high gentisate 1,2-dioxygenase activity. Neither 5-sulfosalicylate nor gentisate-grown cells oxidized 2,6NDS. Therefore, 2,6NDS or an early metabolite must serve as an inducer of the initial catabolic enzyme(s).

Altenbach [12] subjected several naphthalenesulfonates and sulfonate mixtures to the OECD 302 B test and to shaking experiments with test solutions in Erlenmeyer flasks. 1NS and 2NS were only tested in combination with 2,6NDS, 1,5NDS, and 2,7NDS. After a short adaptation phase of 1-3.5 d elimination took place in about 2 d. Even at 10°C, 2NS and 1NS were degraded in 3 and 5 d after an adaptation phase of 5 and 7.5 d, respectively. The observed DOC elimination corresponded to the fraction of both isomers on the original DOC concentration. Therefore, no stable metabolites were observed.

In accordance with [18] in the studies of Altenbach [12] 2,6NDS was relatively readily biodegraded. At 25°C both sludges used were able to degrade 2,6NDS in mixtures in about 3 d after an adaptation phase of about 5 and 13 d, respectively. Even at 10°C 2,6NDS was fully degraded by the sludge acclimated to textile sewage within 28 d. Like for the monosulfonates, the DOC elimination gave no evidence of stable metabolites. 1,5NDS was not biodegraded in any of the experiments. Biodegradation of 2,7NDS was observed with both sludges used, however, the adaptation phases were much longer than for 2,6NDS, differed for single compound solutions and mixtures and depended on prior adaptation of the sludges to 2,7NDS. In summary, Altenbach gave the following order according to the biodegradability of the investigated naphthalenesulfonates: 2NS > 1NS >>2,6NDS > 2,7NDS > 1,5NDS.

Reemtsma et al. [19] carried out biodegradation tests on a mixture of naphthalene- and hydroxynaphthalenesulfonates according to ISO 7827-guideline on ultimate biodegradability. Only 2NS was degraded within 35 d, while the di- and trisulfonated naphthalenes (1,5NDS, 3O2,7NDS, 1O4NS, 1,3,6NTS) remained unaltered.

In good agreement with the above cited literature Fichtner et al. [20] found 1,5NDS and 1,3,6NTS unaltered after an elimination experiment for one week with river Elbe water in a so-called test-filter. 2NS, 2,6NDS, 2,7NDS, and 3O2,7NDS were eliminated during this treatment.

In a recently published paper Neitzel et al. [21] reported on degradation studies on seven naphthalenesulfonates using three different set-ups: (i) a test-filter, (ii) a closed-loop percolation, and (iii) a continuous flow percolation set-up.

The test-filter experiments were carried out at 293 K with river Elbe water and bankside filtered water, spiked with 50 to 100 μg/L of each test substance. Short adaptation times were found in these experiments which varied from 3 to 7 h and the first order rate constants ranged from 0.02 h^{-1} for 4O2,7NDS to 0.6 h^{-1} for 2NS.

The rate constants depended on the structure of the naphthalenesulfonates. The following dependencies were derived:

1. The rate constants decrease with increasing number of sulfonic acid groups and other substituents.
2. Naphthalenesulfonates with a sulfonic acid group and/or other substituents in α-position are degraded more slowly than compounds with an identical structure, but with a sulfonic acid group or a substituent in β-position of the naphthalene moiety.
3. Substituents in α-position reduce the biodegradability more than sulfonic acid groups in the same position.
4. Multiple sulfonation constitutes the worst case for the biodegradability.

The same influence of the chemical structures on the biodegradabilities of naphthalenesulfonates were found in the closed-loop percolation experiments with spiked river Elbe water at 283 K. At this temperature the adaptation times were significantly longer (15 – 40 h) and the rate constants lower (between 0.09 h^{-1} for 4O2,7NDS and 0,12 h^{-1} for 6O4NS).

The third type of degradation experiment which was carried out by Neitzel et al. [21] was a simulation of an accidental spill via a continuous flow percolation set-up. After 3 d of input of the spiked river Elbe water they found a decrease after the first aerobic sediment column between 20 and 50% of the initial naphthalenesulfonate concentrations. Further elimination in the anaerobic part of the column series was marginal.

The poor biodegradability of 1,5NDS was confirmed by field studies of Lange et al. [22]. They monitored the concentrations of 1,5NDS in an industrial test-filter, which uses the secondary effluent of an industrial sewage treatment plant as influent, from February 1993 to November 1995 (22 measurements). The average concentration in the test-filter effluent (0,87 mg/L) was nearly the same as in the influent (0,86 mg/L). The impact of a possible retardation of this compound due to adsorption/desorption was eliminated due to the time integrated data evaluation.

Soeder et al. [23] and Luther et al. [24,25] reported that the green algae Scenedesmus obliquus has a potential to desulfonate naphthalenesulfonates under aerobic conditions.

Soeder et al. [23] expected that the desulfonation of naphthalenesulfonates by microalgae might be relevant also for the degradation of naphthalenesulfonates in natural waters. Using different naphthalenesulfonates as sole source of sulfur, large differences between the test compounds were obtained in the growth rates of Scenedesmus obliquus. The highest growth rate (80% of the growth rate reached with sulfate) was observed for the monosulfonates 1NS and 2NS. Naphthalenedisulfonates, hydroxynaphthalenesulfonates and naphthalenetrisulfonates gave lower growth rates of about 1/6 to 2/3 of the sulfate reference value. The results obtained with naphthalenedisulfonates and hydroxynaphthalenedisulfonates suggested that the degradability increases with decreasing distance between the ligands on the naphthalene ring.

The results of Luther et al. [25] showed that Scenedesmus obliquus can utilize a mixture of 1,3,6- and 1,3,7NTS as the sole source of sulfur. This substance is described as non-degradable by bacteria. After algal desulfonation the bacteria were able to degrade the sulfonate completely. In an open pond the naphthalenetrisulfonate was eliminated with a rate of 9.1 mg/(L · d) in a mixed culture of algae and bacteria. Due to a threshold value of about 17 mg/L 1,3,6-/1,3,7NTS, residuals below this value are expected not to be degraded by an algae/bacteria mixed population. These authors concluded that the degradation of these compounds via the interaction of algae and bacteria would not take place in the Rhine river due to the same reason.

Luther and Soeder [24] studied in detail the availability of 1NS and sulfate as sulfur sources for Scenedesmus obliquus. This green alga was grown in batch cultures either with sulfate or 1NS or both compounds as sulfur source. Growth rates, pigment content and elimination rates of the sulfur compounds were dependent on the initial concentrations of the sulfur sources (K_s-value for sulfate = 9.9 μM; K_s-value for 1NS = 46 μM). Threshold concentrations for uptake were 6.3 μM for sulfate and 38.2 μM for 1NS. When 0.014 – 0.140 mM of sulfate was added to the medium containing 0.217 mM of 1NS, the amount of

1NS eliminated after 5 d was reduced in proportion to the sulfate dosage. The calculated sulfur elimination rates and those obtained using ^{35}S-labeled compounds agreed with one another to a large extent. The carbon of ^{14}C-labeled 1NS did not accumulate in the biomass.

When cultivating Scenedesmus obliquus with sulfate and 1NS as sulfur sources in a turbidostat the maximum growth rate of Scenedesmus obliquus was $\mu = 0.004\ h^{-1}$ and 1NS elimination reached 14%. Additional batch experiments showed that small amounts of sulfate had a great influence on growth and on elimination of 1 NS. Pulse addition of sulfate to a continuous culture with 1NS as sulfur source increased the growth rate 20 times and the elimination rate of 1NS 15 times [24].

2.6.4 Stilbenesulfonates

The behavior of cis-4,4'-dinitro-2,2'-stilbenedisulfonate was also monitored by Lange et al. [22] in an industrial test-filter. Like with 1,5NDS, the average concentration decreased from 3,4 mg/L to 3,1 mg/L. Taking into account the statistical error, no significant degradation was observed.

In the OECD screening test no degradation was observed for the dipotassium salt of 4,4'-dinitro-2,2'-stilbenedisulfonate [26]. This finding agrees well with the observed resistance in the test-filter system [22].

For the free acid of 4,4'-diamino-2,2'-stilbenedisulfonate only 5% degradation was observed in the Zahn-Wellens test and the corresponding disodium salt was not degraded both in the closed bottle test and in the Zahn-Wellens test [26].

2.7 Conclusions

Although PAS are industrially produced and used in large amounts since several decades the data on their physicochemical properties, toxicity, ecotoxicity and biodegradability are quite incomplete and sometimes contradictory.

Log K_{OW} values are missing in many cases, but based on the salt like character of the PAS and the known values for some of these compounds it can be estimated that the bioaccumulation potential of PAS is low.

The biodegradability of a number of PAS were studied. Although different test conditions and organisms were involved in these investigations some general rules become evident. The biodegradability of PAS ranges from easily biodegradable to non-degradable.

Toxic effects caused by long term exposition of organisms to PAS traces in general have not been studied. However, this item is of very importance for a risk assessment, because some PAS are found permanently in sewages and surface waters (see chapter 5). This lack of data very likely is due to the use of many PAS as intermediates and not as consumer products. For a final risk assessment more testings are necessary.

3 Production and uses of polar aromatic sulfonates

3.1 Production volumes of polar aromatic sulfonates

Actual production or consumption volumes of individual PAS are rare in the accessible literature.

In Germany the production volume of 4-methylbenzenesulfonate (p-toluenesulfonate) amounts 5000 tons per year in 1990, calculated as the anhydrous acid [13]. The production volume of this compound was reported to be 25.000 t in Western Europe in the year 1988. For 1985 a total use of 4-methylbenzenesulfonate of 27.000 t is given for Western Europe. 27.8% are converted to the corresponding salts, 26.6% to p-cresol, 2.8% to 2-chlorotoluene-4-sulfonic acid and the remaining 42.8% are applied.

For naphthalenesulfonates one figure was found in an older paper of Noll [27]. Accordingly, in 1976 150,000 tons of naphthalene were converted to naphthalenesulfonic acids.

The *1997 OECD List of High Production Volume Compounds* (HPVC) [28] proved a good tool to find out the technically important PAS from the large number of existing sulfonated compounds. This list contains those chemicals which are produced or imported at levels greater than 1,000 tons per year in at least one OECD Member country. This list has been compiled based upon submissions from 20 Member countries and by combining the European Union's HPV list according to EC Regulation 793/93. It is used by Member countries in choosing chemicals on which to make an initial assessment of their potential to exert a risk to man or environment.

From 4103 records in total 116 aromatic sulfonates or technical mixtures containing them have been extracted (see Appendix in chapter 7). About half of these entries (61 records) have been sorted out as non-relevant for this study. These are compounds like tenside chemicals, lignosulfonates and undefined mixtures, such as sulfonated asphalt. Of the remaining 55 records, which represent the PAS, 30 records contain PAS identified in the aquatic environment and 25 records sulfonated compounds not identified so far. This corresponds to a rate of identification of about 55%.

3.2 Production processes and uses

Production and uses of benzene-, naphthalene-, and anthraquinonesulfonates are described in Ullmann's Encyclopedia of Industrial Chemistry [29][2][30-33]. For more information on the production processes and uses the reader is referred to these references and further literature cited there. In the following, production and uses of some technically important and environmentally relevant PAS are given.

3.2.1 Benzenesulfonates and stilbenesulfonates

3-Nitrobenzenesulfonic acid [30]

Production. 3-Nitrobenzenesulfonic acid is produced by dissolving nitrobenzene in 98% sulfuric acid and heating to 80°C. Then 65% oleum is added at this temperature, and the reaction is completed by heating for 9 h at 105°C. After quenching the sulfonation mass in water, neutralizing with lime, and filtering off gypsum, the calcium salt of the product is converted to the sodium salt with sodium carbonate. After calcium carbonate has been removed by filtration, the sodium salt solution can be used directly or evaporated.

Uses. 3-Nitrobenzenesulfonic acid is used primarily as mild oxidizing agent or as a precursor for colorant intermediates. In the former case it is used in processing certain anthraquinone intermediates, e.g., amination of anthraquinone-1-sulfonic acid to give 1-aminoanthraquinone or as a dye-printing auxiliary to obtain resist effects with, for example, vat dyes. Reduction of 3-nitrobenzenesulfonic acid to the important metanilic acid is achieved with iron or by catalytic hydrogenation.

4-Nitrobenzenesulfonic acid [30]

Production. 4 -nitrobenzenesulfonic acid is produced by hydrolysis of 4-nitrobenzenesulfonyl chloride.

Uses. 4-nitrobenzenesulfonic acid is less important than the ortho and meta isomers because sulfanilic acid (4-aminobenzenesulfonic acid) and its derivatives are readily available from aniline and acetanilide.

3-Aminobenzenesulfonic acid (metanilic acid) [29]

Production. For industrial production of 3-aminobenzensulfonic acid, nitrobenzene is sulfonated to m-nitrobenzenesulfonic acid which is then reduced either with iron or catalytically with hydrogen.

Uses. 3-aminobenzenesulfonic acid is used in the manufacture of dyes and optical brighteners. It is also used to manufacture 3-hydroxybenzenesulfonic acid and 3-aminophenol. The latter is an important intermediate in the manufacture of 4-amino-2-hydroxybenzoic acid (p-aminosalicylic acid) used to fight tuberculosis.

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[2] Because this literature refers to the free acids, the compound names of the corresponding sulfonic acid are used in this subsection.

4-Aminobenzenesulfonic acid (sulfanilic acid) [29]

Production. 4-aminobenzenesulfonic acid is made by the reaction of aniline with sulfuric acid at temperatures above 190°C.

Uses. It is an important intermediate in the production of dyes, pesticides, pharmaceuticals, etc.

4-Hydroxybenzenesulfonic acid [29]

Production. 4-hydroxybenzenesulfonic acid is obtained by sulfonation of phenol with 96% sulfuric acid.

Uses. The crude product obtained by hot sulfonation, i.e., mixed with 2-hydroxybenzenesulfonic acid, is used as such in the manufacture of synthetic tanning agents. Condensation products with formaldehyde improve the dyeing properties of polyamide fibers. 4-Hydroxybenzenesulfonic acid and 2-halogenomalonic esters form the corresponding ethers, which are used in the manufacture of polyesters with improved affinity for basic dyes. If a mixture of hydroxybenzenesulfonic acids and bis(hydroxyphenyl)sulfone is condensed with formaldehyde, and hydrogen sulfite is subsequently added, substances with good dispersing effects on dyes are obtained. They also are used as thinning agents for cement[3]. Most of the 4-hydroxybenzenesulfonic acid is used as an additive for electroplating baths. With ethylene oxide it can be reacted to form poly(ethoxy)oxybenzenesulfonic acid, which can be used as a plasticizer and emulsifier.

4-Methylbenzenesulfonic acid (p-toluenesulfonic acid) [13,29]

Production. 4-methylbenzenesulfonic acid is produced by sulfonation of boiling toluene. For some purposes, for example, for use as an acidic catalyst or in cresol manufacture, the crude toluenesulfonic acid does not have to be purified. Purification is possible by crystallization from 66% sulfuric acid or via the barium salt.

Uses. The application of 4-methylbenzenesulfonic acid includes the manufacture of 4-formylbenzenesulfonic acid, p-sulfobenzoic acid, 2-chlorotoluene-4-sulfonic acid, 4-(chloromethyl)phenylmethanesulfonic acid, and p-cresol. 4-Methylbenzenesulfonic acid is applied mainly as (i) catalyst, (ii) acid for pH adjustment, and (iii) solubilizer and hydrotrope in form of its salts, especially of the sodium salt. For individual applications, see [13].

During the manufacture of 2-chlorotoluene-4-sulfonic acid (3-chloro-4-methylbenzene-sulfonate, see below) this product is not isolated from the reaction mixture of the toluene sulfonation [13]. The mixture is directly chlorinated to give 3-chloro-4-methylbenzenesulfonate, which subsequently is converted to 2-nitro-5-chloro-4-methylbenzenesulfonic acid (2-chloro-5-nitro-p-toluenesulfonic acid). After reduction of the nitro group of 2-nitro-5-chloro-4-methylbenzenesulfonic acid the resulting 2-amino-5-chloro-4-methylbenzenesulfonic acid (2-chloro-5-amino-p-toluenesulfonic acid) is a starting material for pigments (Red 52, Red 53).

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[3] Very likely it must be "plasticizers for concrete" instead of "thinning agents for cement", as reported in [29].

5-Nitro-2-methylbenzenesulfonic acid, 4,4'-dinitro-2,2'stilbenedisulfonate, and 4,4'-diamino-2,2'-stilbenedisulfonate [30]

Production of 5-nitro-2-methylbenzenesulfonic acid. 4-nitrotoluene is sulfonated with 25% oleum at 60°C and worked up to give a solution of the sodium salt of 5-nitro-2-methylbenzene-sulfonic acid.

Uses of 5-nitro-2-methylbenzenesulfonic acid. The most important outlets for this compound exploit the readyness with which it forms stilbene derivatives. Self-condensation products obtained by heating in aqueous sodium hydroxide are used as yellow water-soluble cotton dyes and consist of mixtures containing 4,4'-dinitroso-2,2'-stilbenedisulfonic acid, 4,4'-dinitro-2,2'-stilbenedisulfonic acid and 4,4'-dinitrodibenzyl-2,2'-disulfonic acid.

The entire class of stilbene dyes is based on this chemistry via further reaction of the condensation products, especially 4,4'-dinitro-2,2'-stilbenedisulfonic acid, with aromatic amines or, more usually, with aminoazo compounds to give cheap, water-soluble orange and brown dyes. Manufacture of pure 4,4'-dinitro-2,2'-stilbenedisulfonic acid is achieved by controlled air oxidation in the presence of a catalyst or by oxidation with sodium hypochlorite.

Apart from its use in the production of stilbene dyes, 4,4'-dinitro-2,2'-stilbenedisulfonic acid is more important as the precursor, by Fe-HCl reduction at 100°C, of 4,4'-diamino-2,2'-stilbenedisulfonic acid (flavonic acid), which is the basis for 80% of all fluorescent whitening agents.

3-Chloro-4-methylbenzenesulfonic acid

Concerning the production and uses of 3-Chloro-4-methylbenzenesulfonic acid, see 4-Methylbenzenesulfonic acid.

4-(1-Methylethyl)benzenesulfonic acid (4-isopropylbenzenesulfonic acid, cumene-4-sulfonic acid)

Production. -

Uses. 4-(1-methylethyl)benzenesulfonic acid is used in the textile industry as a hydrotrophic agent [34]

2-Amino-1,4-benzenedisulfonic acid [29]

Production. 2-Amino-1,4-benzenedisulfonic acid is obtained by sulfonating metanilic acid (see 3-aminobenzenesulfonic acid) with 50% oleum at 160°C. It is also possible to start from 4-chloro-3-nitrobenzenesulfonic acid, in which case sulfite is used to replace the chlorine by the sulfonic acid group and the resulting 2-nitro-1,4-benzenedisulfonic acid is then reduced.

Uses. 2-Amino-1,4-benzenedisulfonic acid is used as an intermediate for dyes. It is converted to triazine derivatives, which are intermediates in the manufacture of dyes and optical brighteners.

3.2.2 Naphthalenesulfonates

General production process

Controlled sulfonation starting from naphthalene and using a range of sulfuric acid and oleum strengths under a variety of reaction conditions leads to formation of mono-, di-, tri-, and tetrasulfonic acids, whose separation is frequently complicated by desulfonation (i.e., reverse sulfonation) or isomerization. A common method for isolating naphthalenesulfonic acids and substituted derivatives obtained by sulfonation is the liming-out process. This consists of neutralizing the quenched sulfonation mass (i.e., after addition to excess water) with lime and filtering off the precipitated calcium sulfate while still hot. The solution of the calcium salt of the product is then titrated with sodium carbonate to form the sodium salt. Precipitated calcium carbonate is removed by filtration, and the solution is either evaporated to give the solid sodium salt or used to precipitate a less soluble salt [31].

1-Naphthalenesulfonic acid (naphthalene-α-sulfonic acid) [31]

Production. 1-Naphthalenesulfonic acid is produced by adding naphthalene to 96% sulfuric acid at 20°C and slowly raising the temperature to 70°C. After 3 h at 70-75°C the reaction mass is poured into water and limed out. A technical-grade product is obtained by evaporation and a purer product by precipitating the aniline salt. An alternative sulfonation process uses sulfur trioxide in a solvent such as tetrachloroethane.

Uses. 1-Naphthalenesulfonic acid is further sulfonated or nitrated without isolation. At lower temperature (35°C), sulfuric acid with oleum yields 1,5-naphthalenedisulfonic acid, whereas at higher temperature (100°C) 1,6-naphthalenedisulfonic acid is predominantly obtained. Nitration gives mainly the 5-nitro and 8-nitro derivatives, which are isolated and reduced to the corresponding aminonaphthalenesulfonic acids.

2-Naphthalenesulfonic acid (naphthalene-β-sulfonic acid) [31]

Production. Molten naphthalene is added to 96% sulfuric acid in an iron vessel and the mixture is agitated at 163°C for 2 h. A complex work-up consisting of a gradual dilution, heating, and neutralizing with caustic soda and sodium sulfite ensures an 88% yield of isolated β salt (sodium salt of 2-naphthalenesulfonic acid) and desulfonation of the 1-isomer, which is formed as a co-product in 5 - 10% yield.

Uses. The major outlet for β salt is the production of 2-naphthol. The 2-sulfonic acid is a stage in the production of the 1,6-, 2,6-, and 2,7-disulfonic acids and the 1,3,6-trisulfonic acid. Nitration gives primarily the 5- and 8-nitro derivatives as intermediates for the corresponding aminonaphthalenesulfonic acids (Cleve's acids). Another important outlet for 2-naphthalenesulfonic acid is the condensation with formaldehyde (see 5,5'-, 5,8'-, and 8,8'-methylenebis-2-naphthalenesulfonate) or alcohols to form surface active agents.

1,3-Naphthalenedisulfonic acid [31]
Production. 1,3-Naphthalenedisulfonic acid is produced only in small proportion on disulfonation of naphthalene and cannot be separated. It is prepared in good yield in the laboratory by diazotization and copper-catalyzed deamination of 7-amino-1,3-naphthalenedisulfonic acid.

Uses. No technically important application is known.

1,5-Naphthalenedisulfonic acid (Armstrong acid) [31]
Production. Naphthalene is mixed with 20% oleum at 20-35°C followed by gradual addition of 65% oleum and further naphthalene alternately. After heating for 6 h at 55°C the reaction mixture is added to water, and the product is precipitated as the free acid by cooling or as the disodium salt by the addition of alkaline sodium sulfate. In each case the isolated yield is ca. 53%. The 1,6-disulfonic acid can be recovered from the filtrate. Higher yields of 1,5-naphthalenedisulfonate have been reported for alternative processes; for example, solvent sulfonation with sulfur trioxide and chlorosulfonic acid in a solvent such as tetrachloroethylene or sulfonation with oleum through a double screw-feed apparatus.

Uses. The disodium salt of 1,5-naphthalenedisulfonic acid gives 5-hydroxy-1-naphthalenesulfonic acid or 1,5-dihydroxynaphthalene by fusion processes. Further sulfonation of the disulfonated reaction mixture gives 1,3,5-naphthalenetrisulfonic acid, and nitration leads to 3- and 4-nitro-1,5-naphthalenedisulfonic acids as intermediates to the corresponding aminonaphthalene disulfonic acids. 1,5-Naphthalenedisulfonic acid is also an important stabilizer for diazo compounds.

1,6-Naphthalenedisulfonic acid [31]
Production. Separation from the 1,5-disulfonic acid process (see above) usually meets requirements for the preparation of 1,6-naphthalenedisulfonic acid. It can also be prepared by sulfonation of 2-naphthalenesulfonic acid with oleum, which gives 1,7-naphthalenedisulfonic acid as a byproduct.

Uses. Alkali fusion of 1,6-naphthalenedisulfonate yields 1,6-dihydroxynaphthalene, and sulfonation with oleum produces 1,3,6-naphthalenetrisulfonic acid. However, the main outlet for 1,6-naphthalenedisulfonic acid is via nitration to 8-nitro-1,6-naphthalenedisulfonic acid, which is the intermediate for 8-amino-1,6-naphthalenedisulfonic acid.

1,7-Naphthalenedisulfonic acid [31]
Production. 1,7-Naphthalenedisulfonic acid is produced by sulfonation of 2-naphthalenesulfonic acid with cold oleum to give a mixture of 1,6- (80%) and 1,7- (20%) acids.

Uses. No technically important application is known.

2,6-Naphthalenedisulfonic acid [31]
Production. Naphthalene is added to sulfuric acid-monohydrate ($SO_3 \cdot H_2O$) mixture at 135°C, and the reaction is completed by heating at 170 - 175°C for 5 h. After quenching in water, the disodium salt of 2,6-naphthalenedisulfonic acid is precipitated at 90°C by adding sodium

chloride and sodium sulfate. Filtration at 95°C followed by washing with sodium sulfate solution gives the required product, free from the 2,7-isomer, in 21% yield. The 2,7-isomer is then isolated from the filtrates.

Uses. The disodium salt of 2,6-naphthalenedisulfonate gives 6-hydroxy-2-naphthalenesulfonic acid or 2,6-dihydroxynaphthalene by fusion processes. Nitration of the crude sulfonation product containing 2,6- and 2,7-disulfonic acids gives the 4-nitro derivatives, which, on reduction, give the mixed 4-amino-2,6(2,7)-naphthalenedisulfonic acids (Freund's acid).

2,7-Naphthalenedisulfonic acid [31]

Production. The 2,7-disulfonic acid is always the main product of high-temperature sulfonation of naphthalene, but at 160°C it converts slowly to an equilibrium mixture containing ca. 30% of the 2,6-isomer. Crystallization of the pure product from conventional sulfonation is difficult, and alternative processes, (for example, reaction of naphthalene vapor with sulfur trioxide in the gas phase at 220°C) are said to give a purer product.

Uses. The disodium salt of 2,7-naphthalenedisulfonic acid gives 7-hydroxy-2-naphthalenesulfonic acid or 2,7-dihydroxynaphthalene by fusion processes. Sulfonation by oleum gives the 1,3,6-trisulfonic acid, and nitration gives 4-amino-2,7-naphthalenedisulfonic acid. In sulfuric acid solution, the disodium salt of 2,7-naphthalenedisulfonic acid undergoes an unusual reaction at the 4-position with 4,4'-bis(dimethylamino)benzhydrol. The resulting condensation product is oxidized with lead dioxide to give the acid basic dye C.I. Acid Green 16.

1,3,5-Naphthalenetrisulfonic acid [31]

Production. Naphthalene and 65% oleum are added simultaneously to sulfuric acid monohydrate over a period of 32 h at 30-35°C. The mixture is then heated at 50°C for 1 h, 70°C for 1 h, and finally 90°C for 7 h. This procedure minimizes formation of the 1,3,6-isomer, but a purer product may be obtained by using isolated 1,5-naphthalenedisulfonic acid as starting material.

Uses. The total reaction mixture is nitrated and the resulting 8-nitro derivative is reduced to give a mixture of 8-amino-1,3,5- and 8-amino-1,3,6- naphthalenetrisulfonic acids.

1,3,6-Naphthalenetrisulfonic acid [31]

Production. Naphthalene is initially sulfonated with sulfuric acid monohydrate under programmed temperature control between 80 and 145°C. Then, 65% oleum is added gradually at 40°C and heating is continued for 2.5 h at 145°C. Trisulfonation is complete after the further addition of 65% oleum and heating for 3 h at 150°C. This complex procedure maximizes the formation of 1,3,6-naphthalenetrisulfonic acid with a conversion of up to 75%.

Uses. The total reaction mixture is nitrated, and the resulting 8-nitro derivative is reduced to give 8-amino-1,3,6-trisulfonic acid (Koch acid), the key intermediate in the production of the important H acid (4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid). The crude trisodium salt may be precipitated from the quenched mixture after dilution to 75% acid strength to give a product (Azoguard) used as a diazo stabilizer.

1,3,7-Naphthalenetrisulfonic acid [31]

Production. 1,3,7-Naphthalenetrisulfonic acid is much less important than the 1,3,5- and 1,3,6-isomers. It is produced by sulfonation of 2,6-naphthalenedisulfonic acid with 65% oleum in sulfuric acid monohydrate.

Uses. No technically important application is known.

Methylenebis-2-naphthalenesulfonic acid (5,5'-, 5,8'-, and 8,8'-isomer)

Production. Condensation of sodium 2NS with formaldehyde gives the dimer methylenebis-2-naphthalenesulfonic acid or polymeric condensation products [31].

Uses. These condensation products (sulfonated naphthalene-formaldehyde condensates SNFC) are important as plasticizers for concrete [35-38], synthetic tanning agents [39,40] and dispersants [41,42].

2-Amino-1,5-naphthalenedisulfonic acid (5-sulfo-Tobias acid) [31]

Production. Sulfonation of 2-amino-1-naphthalenesulfonic acid (Tobias acid) to produce 6-amino-1-naphthalenesulfonic acid proceeds via 2-amino-1,5-naphthalenedisulfonic acid, with careful avoidance of desulfonation.

Uses. 2-Amino-1,5-naphthalenedisulfonic acid is used as a diazo component in orange and red reactive dyes. It gives more bathochromic shades than Tobias acid.

3-Amino-1,5-naphthalenedisulfonic acid (Cassella acid, C acid)[31]

Production. The iron(II) salt of 3-nitro-1,5-naphthalenedisulfonic acid (nitro-Armstrong acid) is reduced with iron in dilute acid. A claimed improvement involves isolation of nitro-Armstrong acid from the nitration products of 1,5-naphthalenedisulfonic acid as the crystalline magnesium salt prior to catalytic reduction to 3-amino-1,5-naphthalenedisulfonic acid.

Uses. 3-amino-1,5-naphthalenedisulfonic acid is an important diazo component for yellow direct and reactive dyes.

7-Amino-1,3-naphthalenedisulfonic acid (amino G acid)[31]

Production. The disodium or dipotassium salt of 7-hydroxy-1,3-naphthalenedisulfonic acid is heated with excess aqueous ammonia and ammonium bisulfite at 185°C for 18 h. The reaction mixture is basified, heated to remove excess ammonia, neutralized, and evaporated while any residual sulfite is removed.

Uses. The amino G acid liquor (95% yield) resulting from its production is used directly for caustic fusion to give 6-amino-4-hydroxy-2-naphthalenesulfonic acid (γ acid), the major outlet.

3-Hydroxy-2,7-naphthalenedisulfonic acid (R acid)[31]

Production. 2-Hydroxynaphthalene is heated in excess 98% sulfuric acid to 60°C, and anhydrous sodium sulfate is added. The mixture is then heated for 24 h at 105°C, 12 h at 110°C, and 12 h at 120°C before being diluted with more sulfuric acid and quenched in water. Sodium chloride is added at 60°C, and the mixture is cooled slowly to 30°C with crystallization of the product as its sodium salt. The isolated yield is 68%, and the product contains about 3% of sodium 2-hydroxy-6-naphthalenesulfonate (Schaeffer's salt) as the major impurity. Alternatively, R salt may be recovered as a byproduct from the G acid process (see below). Further purification may be effected via the aniline salt.

Uses. The so-called R acid is used as a coupling component for a wide range of azo colorants, e.g., C.I. Mordant Red 9, C.I. Pigment Red 60, C.I. Acid Red 27, and C.I. Food Red 9. The aluminium salt of R acid has been used as an astringent and antiseptic (Alumnol).

4-Hydroxy-2,7-naphthalenedisulfonic acid (RG acid, Violet acid) [31]
Production. 1,3,6-Naphthalenetrisulfonic acid is heated with 50% sodium hydroxide at 180°C for 15 h in an autoclave. After dilution with water, the product is salted out as the monosodium salt and purified by washing with brine.

Uses. 4-hydroxy-2,7-naphthalenedisulfonic acid is used as a coupling component for azo dyes, e.g., C.I. Acid Red 7.

7-Hydroxy-1,3-naphthalenedisulfonic acid (G acid) [31]
Production. 2-hydroxynaphthalene is added to 98% sulfuric acid at 40°C. Then, 20% oleum is added over 6 h and the temperature is allowed to rise to 60°C. The reaction is completed by heating for further 16 h at 60°C followed by 15 h at 80°C. After the reaction mixture has been poured into water, potassium chloride is added to the hot solution and the batch is cooled slowly to 35°C before filtering off the crystalline dipotassium salt of G acid and carefully washing out any residual R salt (see above); the yield is 60%. In addition R salt can be recovered from the filtrate in 12% yield after conversion to its sodium salt.

Uses. The G acid is aminated (Bucherer reaction) to give 7-amino-1,3-naphthalenedisulfonic acid and subjected to caustic fusion at 200°C to yield 4,6-dihydroxy-2-naphthalenesulfonic acid (a precursor of γ acid). It is also used as a coupling component for a wide range of azo colorants, e.g., C.I. Acid Orange 10, C.I. Acid Red 187, and Food Red 7.

3.2.3 Anthraquinonesulfonates and other sulfonates

2-anthraquinonesulfonic acid [32,43]

Production. 2-anthraquinonesulfonic acid is obtained by sulfonation of anthraquinone with oleum at 160°C. It can also be obtained from 1,6- or 1,7-anthraquinonedisulfonic acid via desulfonation of the sulfonic acid group in 1-position.

Uses. 2-anthraquinonesulfonic acid is an intermediate in the production of anthraquinone dyes.

1,8-anthraquinonedisulfonic acid [32]

Production. 1,8-anthraquinonesulfonic acid is produced via sulfonation of naphthalene in the presence of mercury. The 1,5- and 1,8-disulfonic acids are separated by stepwise salting out or by slowly diluting the reaction mixture with diluted sulfuric acid or water. The isomer ratio can be controlled to some extent through the choice of the reaction conditions.

Uses. 2-anthraquinonesulfonic acid is an intermediate in the production of anthraquinone dyes.

1-amino-4-bromo-2-anthraquinonedisulfonic acid [32]

Production. -

Uses. 2-anthraquinonesulfonic acid is an intermediate in the production of anthraquinone dyes.

No data were available for ***4,4'-diamino-1,1'bianthraquinone-3,3'-disulfonic acid*** and *2-hydroxy-4,6-bis(4-sulfanilo)-1,3,5-triazine.*

3.3 Conclusions

For most of the PAS considered there is information available on their production processes and their uses. However, precise production and consumption volumes are not accessible in the open literature, except for a few compounds. As the *OECD List of High Production Volume Compounds* compiles those chemicals which are produced or imported in amounts larger than 1,000 tons per year, it serves as a good tool in order to select PAS, which can be expected to occur in the aquatic environment.

4 Methods of analysis for the trace-level determination of polar aromatic sulfonates

The trace-analytical methods for the determination of PAS were reviewed by Reemtsma [44]. Following this paper the published methods of analysis are divided up into two classes of approaches:

- procedures for the less polar LAS and related compounds, i.e. dialkyltetralin sulfonates (DATS) and sulfophenyl carboxylates (SPC) and
- procedures for polar sulfonates.

The so-called PAS in the above mentioned review [44] cover the same group of compounds as this survey does and, therefore, here the extraction and separation techniques have to be discussed only for these compounds. The review by Reemtsma is a complete compilation of the relevant methods of analysis before 1996. Therefore, in order to avoid rewriting of this paper, the relevant text sections of Reemtsma's review are given in the following with a few marginal changes.

4.1 Extraction of polar aromatic sulfonates

Solid-phase extraction (SPE), applied to LAS, is less suitable for more polar compounds lacking a hydrophobic alkyl chain such as naphthalenesulfonates, benzenesulfonates, and their amino- and hydroxy-derivatives. With K_{ow}-values up to four orders of magnitude below the values for LAS, these substances exhibit no retention on C_{18} reversed-phase material. However, SPE is suitable if these sulfonates are paired with an organic cation such as tetraalkylammonium. Ion-pair formation with methylene blue [45] or tetrabutylammonium (TBA) [46,47] was also used for liquid-liquid extraction (LLE) of polar sulfonates and dyes.

Miyoshi et al. [48] invented the combination of ion-pairing (with cetyltrimethylammonium, CTMA) and solid-phase extraction (SPE) for the extraction of aminonaphthalenesulfonates from aqueous environments. Schullerer et al. [49] used TBA to extract eleven sulfonates and disulfonates from standard solutions. Recoveries were lowest for nitro- and diamino-substituted sulfonates (50-72%), while benzenesulfonates and naphthalenesulfonates reached 100%. The method was applied to surface water, bankside filtered water, and secondary effluents.

Brouwer et al. [50] implemented ion-pair extraction in their on-line trace enrichment system with PLRP-S. Recoveries were almost quantitative except for amino-substituted sulfonates (70-80%). However, interference from humic substances was observed, which was reduced by the addition of sodium chloride prior to extraction, but this affected the recovery of the most polar sulfonates. Ion-pairing with CTMA was reported [51], and recovery rates in the range of 80-110% from river water were obtained. With the more hydrophobic CTMA instead of TBA, amino-substituted sulfonates appear to be more effectively extracted [51].

Ion-pair SPE with TBA of various sulfonates worked poorly with spiked industrial wastewater of unknown source, though it worked well with synthetic samples [52]. Extraction of sulfonated polyphenols with TBA from tannery wastewater was not negatively affected by salt contents up to 20 g/L [53].

Usually, the ion-pairing agent is added to the aqueous sample prior to extraction. Alternatively, Zerbinati and Ostacoli [54] saturated the solid-phase with octyltrimethylammonium acetate, thereby producing an ion-exchange column, and applied the sample afterwards. Several anthraquinonesulfonates and -disulfonates, naphthalenedisulfonates, and hydroxynaphthalenedisulfonates were obtained from standard solutions with 80-120% recovery, but the ion-exchange capacity and the breakthrough volume were low. The authors observed anthraquinonesulfonates to be incompletely desorbed from C_{18} cartridges, when the CTMA-cation was employed.

Lange et al. [55] determined eleven aromatic sulfonates, some of them being substituted with amino-, hydroxy- and nitromoieties, by on-line ion-pair extraction on C_{18} material and applied this method to surface water and bank filtrate, media which are not hampered by high salt contents. Again, extraction of amino-substituted sulfonates proved problematic. Although being a valuable tool for the extraction of aromatic sulfonates from aqueous media, ion-pair SPE suffers from three major drawbacks.

i. Co-extraction of interfering dissolved organic compounds is an even larger problem in ion-pair SPE than in conventional reversed phase SPE (RP-SPE) [52]. Thus, the need for sample clean-up prior to analysis is more urgent. The lack of interaction between PAS and C_{18}-material allows the use of a C_{18}-cartridge for the removal of less polar substances prior to ion-pair extraction [48,51,52].

ii. It exhibits limited extraction efficiency for very polar sulfonates, namely amino- and amino-hydroxy-substituted derivatives [55]. The breakthrough volumes might be low when employing TBA as cation [56]. The use of CTMA might help to some extent [54].

iii. High contents of inorganic salts might substantially affect recoveries. While a supporting salting-out effect is observed in conventional RP-SPE of LAS, inorganic anions compete with the sulfonate ions for the organic cation, thereby decreasing the extent of ion-pair formation of the sulfonates and their extraction efficiency. This is of concern in the analysis of industrial wastewater [52] and would hamper the extraction from seawater.

An alternative approach avoiding some of these problems was presented by Altenbach and Giger [56]. They revealed that deactivated charcoal (Carbopack B) is also suitable for the specific extraction of PAS from industrial and domestic wastewater without ion pairing. Like Di Corcia et al. [57], they suggested ionic interactions to be responsible for the specific adsorption of anionic species, thereby reducing the interference from humic substances. Ion-pair reversed phase liquid chromatography (RPLC) analysis could be performed without an intermediate clean-up. However, elution of aminosulfonates was difficult. Interferences by elevated salt contents appear to be weaker on Carbopack B than on ion-pair SPE. Chemically modified polystyrene-divinylbenzene resins [58], which have now become commercially available, might also offer suitable extraction properties for PAS.

Extraction of PAS by anion-exchange phases was unsuitable. While the extraction might be complete, polysulfonated aromates are only incompletely eluted from these phase [52,56]. Tsukioka [59] obtained 86-95% recovery of 0.2 µg/L amounts of anthraquinonesulfonates from spiked river water with a weak anion exchange column. Lyophilization, followed by resolution in methanol and precipitation of inorganic salts by addition of acetone might be suitable for the preparation of single extracts [60].

4.2 Ion-pair reversed-phase liquid chromatography with polar aromatic sulfonates

With increasing polarity of the sulfonates, e.g., due to substitution with amino- and hydroxy-groups or to polysulfonation, the interaction of the analytes with the reversed-phase column becomes too weak to obtain separation. Although separation of benzenesulfonates, aminonaphthalenesulfonates, hydroxynaphthalenesulfonates, other monosulfonates and dyes by RPLC was achieved with high inorganic modifier concentrations [61,62], ion-pair RPLC has become the method of choice. Since its invention, the underlying mechanisms have been a matter of debate. The following two fundamental retention mechanisms are proposed.

i. The *ion-exchange mechanism.* Assuming that the stationary phase is saturated with the organic cation continuously delivered with the mobile phase, the analytes are separated according to the strength of ionic interaction with the fixed organic cation [63,64].

ii. The *ion-pair formation and hydrophobic interaction.* A two step retention mechanism is suggested: first, the sulfonates form ion-pairs with the organic cation dissolved in the mobile phase; secondly, these ion-pairs are separated due to hydrophobic interaction with the stationary phase [65]. Retention thus depends on the strength of ion-pair formation and the affinity of the ion-pairs towards the stationary phase.

Experimental evidence for both mechanisms was obtained [65,66]. Indeed, they might represent the pure theoretical extremes of the actual situation.

For further details about the factors influencing ion-pair RPLC see [44] and the references cited there.

4.3 Application to environmental analysis

While studies on the factors influencing ion-pair RPLC of aromatic sulfonates are frequently published, its application in environmental analysis is, although now increasing, still comparatively rare. Miyoshi et al. [48] reported the separation of several aminonaphthalenesulfonates extracted from waters and sediments. Schullerer et al. [49] analyzed sulfonated aromatic compounds in surface water, bankside filtered water, and secondary effluents. Several signals were detected by means of UV and fluorescence detection, but only one of them could be ascribed to a certain compound. Brouwer et al. [50] provided an example of surface water monitoring with an ion-pair modification of their on-line trace enrichment system and identified an anthraquinonedisulfonate in River Rhine water after an accidental spill in Germany. They reported detection limits of 0.2-3 µg/L from a sample volume of 30 mL.

Zerbinati et al. [51,54] identified several aromatic sulfonates in river water by means of ion-pair RPLC with CTMA on a C_8-phase. The detection limits were in the range of 1-60 µg/L and some sulfonates were still unidentified. Reemtsma et al. [53] determined sulfonated polyphenols in tannery wastewater and the secondary effluent of a pilot plant.

In 1995 more extensive work on the determination of PAS was reported. Lange et al. [55] developed an automated system of on-line ion-pair extraction and ion-pair RPLC and obtained detection limits of 0.05-2 µg/L from sample volumes of 50 mL. With this system, biologically treated wastewater, surface water, and waters from various steps of drinking water treatment, such as bankside filtration, ozonation, and activated charcoal adsorption, were analyzed. 1,5NDS was identified as a dominant and persistent pollutant.

Altenbach and Giger [56] analyzed 25 sulfonates and 8 carboxylic acids by ion-pair RPLC. Combined with SPE on Carbopack B, they applied this method to industrial wastewater, a wastewater treatment plant influent and effluent, as well as to surface water. Detection limits were in the range of 0.1-1 µg/L from sample volumes of 100 mL. Nine PAS were identified in a wastewater treatment plant, which was dominated by wastewater from the textile industry.

4.4 Conclusions

Trace-analytical methods for PAS, which are sensitive and selective enough for environmental analysis, e.g. for monitoring of PAS concentrations in raw waters of water works or in drinking water are nowadays available. However, standardized methods (CEN; ISO, EPA) do not exist and the elaboration of those methods is recommended.

5 Occurrence of polar aromatic sulfonates in the aquatic environment

PAS have been identified and quantified in a number of different waters. The majority of data was obtained from surface waters and especially from river waters.

5.1 Occurrence of polar aromatic sulfonates in landfill leachates and groundwaters

5.1.1 Occurrence of polar aromatic sulfonates in landfill leachates

Only two papers have been found on the occurrence of PAS in landfill leachates [12,67]. Altenbach [12] quantified ten PAS in three samples from the waste dump site Tännlimoos (Canton Zug, Switzerland). Besides 4-amino-1-naphthalenesulfonate he identified eight naphthalene- and aminonaphthalenesulfonates, and 2-amino-5-chloro-4-methylbenzenesulfonate (CLT acid) as sole benzenesulfonate. Their concentrations are given in Table 5-1. This dump site is predominantly filled with construction waste and bottom ashes of waste incinerators. Because no PAS could be found in the bottom ashes, he concluded that the probable source of the naphthalenesulfonates are sulfonated naphthalene-formaldehyde condensates (SNFC) used as concrete admixtures (superplasticizers). The source of the aminonaphthalenesulfonates and the CLT acid is also not clear, but an anaerobic cleavage of azo dyes was discussed.

Table 5-1: Polar aromatic sulfonates in leachates from the waste dump site Tännlimoos, Switzerland [12]

compound	**sample 1**[a]	**sample 2**[a] concentration in µg/L	**sample 3**[b]
benzenesulfonates			
2-amino-5-chloro-4-methylbenzenesulfonate	60 -80	5 – 10	bd
naphthalenesulfonates			
1-naphthalenesulfonate	10	1 – 2	2.6
2-naphthalenesulfonate	20	2 – 3	9.9
1,5-naphthalenedisulfonate	10	bd	bd
1,6-naphthalenedisulfonate	10 - 15	bd	0.7
2,6-naphthalenedisulfonate	bd	bd	0.3
2,7-naphthalenedisulfonate	10 -15	bd	1.2
4-amino-1-naphthalenesulfonate	5	bd	bd
2-amino-1,5-naphthalenedisulfonate	5 - 10	bd	bd
3-amino-1,5-naphthalenedisulfonate	15 - 20	bd	bd

[a] determined with UV detection

[b] determined with fluorescence detection

bd below detection limit

Menzel [67] analyzed samples from the waste dump sites Karlsruhe-West and Grötzingen, both situated in Karlsruhe, Germany, for naphthalenesulfonates and SNFC. Smaller SNFC up to a degree of condensation of four methylene-bridged 2-naphthalenesulfonate units have been identified in the leachates from the two waste dump sites investigated. The corresponding concentrations of the non-condensed naphthalenesulfonates were found to be of the same order of magnitude as the values given by Altenbach, but these numbers need additional confirmation.

5.1.2 Occurrence of polar aromatic sulfonates in groundwaters

There are no reports in the literature on the analysis of PAS in the raw water of water works using groundwater.

5.2 Occurrence of polar aromatic sulfonates in sewage

There is only a limited number of papers on the occurrence of PAS in sewage or during sewage treatment [12,19,22,56,68-70]. Table 5-2 shows the compounds identified in these investigations. Nearly all available data from quantitative measurements on treated sewage are taken from publications of Altenbach [12], Altenbach and Giger [56] and Lindner et al. [68]. The only measurements on corresponding influent and effluent samples were carried out by Altenbach [12].

Table 5-2: Polar aromatic sulfonates identified in different sewages

	sewage treatment plant	**influent in µg/L**	**effluent in µg/L**	**reference**
benzenesulfonates				
3-aminobenzenesulfonate	H	13 - 1280	1 – 381	[12,56]
2-amino-1,4-benzenedisulfonate	H	nq	nq	[12]
3-nitrobenzenesulfonate	H	bd - 3438	bd –1286	[12,56]
4-nitrobenzenesulfonate	H	bd - 208.3	bd - 49.9	[12,56]
4-(1-methylethyl)benzenesulfonate	H	nq	nq	[12,56]
4-hydroxybenzenesulfonate	H	nq	nq	[12]
2-amino-5-chloro-4-methylbenzenesulfonate	IS[a)]	nd	19 – 2000	[68]
naphthalenesulfonates				
1-naphthalenesulfonate	H	0.09 - 55.4	bd – 10.7	[12,56]
2-naphthalenesulfonate	H	0.8 - 298.6	bd - 106.9	[12,56]
1,3-naphthalenedisulfonate	IS[a)]	nd	0.8 – 88	[68]
1,5-naphthalenedisulfonate	IS[a)]	nd	9.4 – 3200	[68]
	IS	nd	870 (22)[b)]	[22]
	H	0.1 - 18.7	0.3 - 7.0	[12,56]
	IS	nd	80 – 600	[69]
1,6-naphthalenedisulfonate	IS[a)]	nd	1.6 - 7.8	[68]
	H	0.8 - 85.3	0.3 - 35.0	[12,56]
1,7-naphthalenedisulfonate	IS[a)]	nd	2.7 – 19	[68]
	H	nq	nq	[12]
2,6-naphthalenedisulfonate	IS[a)]	nd	1.2 - 2.5	[68]
	H	0.13 - 8.3	bd - 3.6	[12,56]
2,7-naphthalenedisulfonate	IS[a)]	nd	0.4 – 57	[68]
	H	0.3 - 26.4	0.1 - 10.6	[12,56]
1,3,5-naphthalenetrisulfonate	IS[a)]	nd	12 – 79	[68]
1,3,6-naphthalenetrisulfonate	IS[a)]	nd	13 – 120	[68]
methylenebis-2-naphthalenesulfonate	P	nd	90 – 110	[71]
(5,5'-, 8,8'- and 5,8'-isomers)	T	nd	2.8 - 3.4	[71]
	PM	nd	0.14 - 0.16	[71]
	M	nd	0.38 - 0.77	[71]
2-amino-1,5-naphthalenedisulfonate	H	nq	nq	[12,56]

	sewage treatment plant	influent in µg/L	effluent in µg/L	reference
3-amino-1,5-naphthalenedisulfonate	IS[a]	nd	9.0 – 130	[68]
	H	nq	nq	[12,56]
3-hydroxy-2,7-naphthalenedisulfonate	IS[a]	nd	9.6	[68]
anthraquinonesulfonates				
1,8-anthraquinonedisulfonate	IS[a]	nd	390 – 870	[68]
stilbenesulfonates				
cis-4,4'-diamino-2,2'-stilbenedisulfonate	IS[a]	nd	630 – 2600	[68]
trans-4,4'-diamino-2,2'-stilbenedisulfonate	IS[a]	nd	2700	[68]
cis-4,4'-dinitro-2,2'-stilbenedisulfonate	IS[a]	nd	950 – 6500	[68]
	IS	nd	3400 (22)[b]	[22]
other sulfonates				
2-Hydroxy-4,6-bis(4-sulfanilo)-1,3,5-triazine	IS[a]	nd	51 – 670	[68]

[a] summary of data for three non-specified chemical companies

[b] average (number of measurements in brackets)

bd	below detection/determination limit	IS	industrial sewage treatment plant
nq	not quantified	M	municipal sewage treatment plant
nd	no data	P	SNFC producing company
H	municipal sewage treatment plant in Herisau, Switzerland,	PM	pulp mill
		T	tannery

Lindner et al. [68] identified 16 PAS, one benzenesulfonate, ten naphthalenesulfonates, one anthraquinonesulfonate, three stilbenesulfonates and one sulfonated hydroxytriazine compound in secondary effluents of three companies of the chemical industry by ion-pair HPLC with UV and fluorescence detection. Their occurrence in secondary effluents demonstrates the persistence of PAS. The highest concentrations in the low mg/L range were reported for 2-amino-5-chloro-4-methylbenzenesulfonate, 1,5NDS, cis-4,4'-dinitro-2,2'-stilbenedisulfonate and cis- and trans 4,4'-diamino-2,2'-stilbenedisulfonate. Except for the trans-4,4'-diamino-2,2'-stilbenedisulfonate all other compounds have also been found in the River Rhine (see below), the receiving water body. The industrially produced trans-stilbenes are mainly transformed by sunlight into the corresponding cis-isomers within hours [22,72]. Therefore, usually only the cis-isomers are found in environmental samples. Trans-4,4'-diamino-2,2'-stilbenedisulfonate was identified only in a colored industrial sewage [68].

The studies of Altenbach [12] are complementary to the results of Lindner et al. [68], because a different extraction procedure was applied. The off-line extraction with Carbopack B® solid-phase material applied by Altenbach [56] gives better recoveries for the polar amino- and hydroxybenzenesulfonates and, therefore, allows their quantitative determination in sewages, whereas the on-line ion-pair extraction with RP-C18 material is well suited for routine analysis of the less polar benzenesulfonates, naphthalenesulfonates and especially for amino- and hydroxynaphthalenesulfonates [55], which are not amenable to Carbopack B® extraction.

Altenbach [12] studied in detail the elimination of benzene- and naphthalenesulfonates from the textile industry discharged into the municipal sewage treatment plant of Herisau, Switzerland. This plant receives approximately 50% of industrial waste waters from the three major textile manufacturing and finishing plants Signer AG, Walser AG, and Zilander AG. Under almost optimum conditions, i.e. acclimated activated sludge and moderate dry weather flows, he found elimination rates of 98% and 96% for 3NBS and 3ABS, respectively, in the Herisau sewage treatment plant. Loads of up to 70 kg per day calculated as 3NBS were determined. The fractions of 3NBS and 3ABS varied strongly in the course of a week and shifted from below 20% of 3ABS at the beginning up to 100% at the end of the week. This repeatedly observed effect was ascribed to an abiotic reduction of 3NBS during anaerobic pretreatment in the storage tanks of the textile industry. 4NBS was determined as minor impurity of 3NBS with a relative amount between 4% and 6% in the sum of both nitrobenzenesulfonates. Its reduced form could not be quantified due to chromatographic interferences.

The isomer patterns, concentrations and massfluxes of six naphthalenesulfonates have also been investigated in the Herisau sewage treatment plant [12]. In the influent the ratio of the sum of monosulfonates (1NS and 2NS) and the sum of the four quantified naphthalenedisulfonates (1,5NDS, 1,6NDS, 2,6NDS and 2,7NDS) varied between 60% and 80%. These relatively high variations indicate that the naphthalenesulfonates did not originate from a single source. The isomer ratios were found to be nearly constant within the group of monosulfonates (87 ± 2% 2NS, 13 ± 2% 1NS) and also within the group of disulfonates (12 ± 3% 1,5NDS, 62 ± 2% 1,6NDS, 6 ± 1% 2,6NDS and 20 ± 3% 2,7NDS). No systematic increase or decrease was observed during the course of a week. Therefore, there was no evidence for an elimination or transformation of naphthalenesulfonates in the mostly anaerobic waste water storage tanks of the textile industry. The small concentrations of less than 300 µg/L 2NS suggest that these compounds were introduced by the application of sulfonated naphthalene-formaldehyde condensates (SNFC). The variations could then be explained by different condensation grades of SNFC products applied in the textile industry.

Krull and Hempel [73] studied the degradation of 1NS, 2NS, 1,5NDS, 1,6NDS, 2,6NDS, 2,7NDS and 6-amino-2-naphthalenesulfonate in a two-stage laboratory plant with specially adapted and immobilized microorganisms fixed on broken sand particles. The plant consisted of two coupled airlift-loop reactors. In the first stage the sequential metabolization of 2NS and 1NS was achieved by strain Pseudomonas testosteroni A3 at residence times down to 1.5 h. The total degradation of the remaining 1NS and the recalcitrant naphthalenesulfonates was obtained by a defined mixed culture in the second unit. Non-biodegradable 1,5NDS was the main component in the effluent. These authors further observed a considerable inhibition of the biological degradation in the second unit with salt, i.e., Na_2SO_4, loaded wastewater.

Table 5-3 shows the eliminations found out during the aerobic sewage treatment [12,73].

Table 5-3: Elimination in % of naphthalenesulfonates in a field study (Herisau, Jan. 31 - Feb. 5, 1994, [12]) and in a two-step laboratory sewage treatment plant, [73]

	laboratory treatment plant					Herisau
	1st stage with salt	**2nd stage with salt**	**2nd stage without salt**	**both stages with salt**	**both stages without salt**	**treatment plant**
1NS	23	59	100	70	100	100
2NS	96	100	100	100	100	100
1,5NDS	0	0	0	88	0	4
1,6NDS	0	88	100	88	100	96
1,7NDS	nd	nd	nd	nd	nd	5
2,6NDS	0	39	100	39	100	95
2,7NDS	nd	nd	nd	nd	nd	78

nd: no data

The data presented in table 5-3 agree well between both studies. The large differences in the elimination of these structurally very similar compounds is also treated in subchapter 2.6 "Biodegradability data".

Reemtsma et al. [19] did not observe any elimination of 1,5NDS, 1,3,6NTS, 4-hydroxy-1-naphthalenesulfonate and 3-hydroxy-1,7-naphthalenetrisulfonate in a tannery wastewater treatment pilot plant. Only 2NS was eliminated after 35 days.

Redín et al. [71] identified three 2:1 condensates of 2NS and formaldehyde (2:1 SNFC) in the wastewater of a concrete admixtures producing company, a tannery, a pulp mill and a sewage treatment plant. The identification was possible after regio-controlled synthesis of the reference compounds 5,5'-, 5,8'- and 8,8'-methylenebis-2-naphthalenesulfonate. The highest concentrations were observed in the effluent of a producing company where between 90 µg/L and 110 µg/L were determined for each isomer. The isomer ratio was about 1:1:1.

The oligomeric SNFC identified by Redín et al. are very likely identical with the unknown group of naphthalene based compounds reported by Altenbach [12]. Further studies on the elimination of SNFC in sewage treatment are missing.

No systematic investigation was found in the literature on the occurrence of PAS in sewage sludges, soil, suspended solids, and sediments. Only Altenbach [12] reported on the qualitative occurrence of 2- and 3-amino-1,5-naphthalenedisulfonate in the Herisau sewage treatment plant.

5.3 Occurrence of polar aromatic sulfonates in surface waters

Measurements in surface waters for PAS were carried out exclusively on river and creek water. Lakes have not been studied so far. In table 5-4 the sulfonates identified in these waters are compiled together with the measured concentration or concentration ranges. The data in this table should give an impression of the order of magnitude of PAS concentrations in rivers. They are not the result of a statistical data evaluation. This seems to be nearly impossible, because there are two many differences between the papers, i.e., different sampling, different detection or determination limits etc.

Most of the published monitoring data are related to German rivers, especially to the Rhine and Elbe rivers, although in other European countries some first investigations were carried out, e.g., on the Danube river and its tributaries and on a small river in North West Italy, the Bormida river. Further investigations on the Czech part of the Elbe river are subject of a current research project.

The figures 5-1 to 5-4 show the concentrations of 1,5NDS, 2-amino-1,5-naphthalenedisulfonate, 3-amino-1,5-naphthalenedisulfonate and cis-4,4'-dinitro-2,2'-stilbenedisulfonate in the Rhine river during the last years. These four not readily biodegradable compounds are frequently measured in the Rhine river in concentrations above their determination limit [74-78].

The highest concentrations in the Rhine river were measured for 1,5NDS and cis-4,4'-dinitro-2,2'-stilbenedisulfonate at a sampling site in Düsseldorf. In the first two years, 1992 and 1993, the concentrations of 1,5NDS decreased significantly to a level between approximately 0.5 and 3 µg/L. The concentration of cis-4,4'-dinitro-2,2'-stilbenedisulfonate is expected to increase in the next years, because Bayer AG in Leverkusen has recently installed a new production plant for fluorescent whitening agents (Blankophore®) on the basis of flavonic acid (4,4'-diamino-2,2'-stilbenedisulfonate), which is produced from 4,4'-dinitro-2,2'-stilbenedisulfonate [79].

Typical concentrations found for PAS in larger rivers range from a few tens ng/L up to several µg/L. In the Elbe river sometimes concentrations up to several tens of µg/L were observed for different naphthalenesulfonates. Higher values up to the g/L level are only reported in one paper [51] and probably can be attributed to a high percentage of wastewater in the Bormida river.

The most widespread occurring group of PAS are the naphthalenesulfonates. Mono-, di-, and trisulfonates seem to be ubiquitarily distributed in anthropogenic influenced rivers. These compounds originate both from production sites and from their multiple applications. One important source are technical mixtures of naphthalenesulfonates with formaldehyde, which are used, e.g., as synthetic tanning agents and in many other applications as dispersants. Concerning the Rhine river, the simultaneous occurrence of the monomeric naphthalenesulfonates together with dimeric condensation products 5,5'- 5,8'-, and 8,8'-methylenebis-2-naphthalenesulfonate supports this explanation [22,77,78].

The occurrence of some individual compounds, such as 1,5NDS, 1,8-anthraquinonedisulfonate, 5-nitro-2-methylbenzenesulfonate, cis-4,4'-dinitro-2,2'-stilbenedisulfonate, 2-hydroxy-4,6-bis(4-sulfanilo)-1,3,5-triazine and the benzenesulfonates 3-chloro-4-methylbenzenesulfonate and 2-amino-5-chloro-4-methylbenzenesulfonate could be ascribed with a high probability to regular or accidental spills of certain producers [22,50,55,80,81].

Table 5-4: Polar aromatic sulfonates identified in different rivers

	river	**concentration in µg/L**[a]	**reference**
benzenesulfonates			
3-aminobenzenesulfonate	B	15 – 940 000	[51]
4-aminobenzenesulfonate	B	1.5 – 410 000	[51]
3-nitrobenzenesulfonate	LC-trib	27	[82]
	R	0.3 – 1.2	[12]
5-nitro-2-methylbenzenesulfonate	R	1.8 – 4.1	[80]
3-chloro-4-methylbenzenesulfonate	M	≤ 2.3	[22]
	S/R	≤ 1.1	[83]
2-amino-5-chloro-4-methylbenzenesulfonate	M	≤ 5.0	[22]
	R	1.0 – 1.2	[74]
	S/R	≤ 6.2	[83]
naphthalenesulfonates			
1-naphthalenesulfonate	B	6.5 – 1 570 000	[51]
	E	2.3 (9)[b]	[21]
	LC-trib	≤ 0.2	[82,84]
	R	≤ 0.09	[75-78,82,84]
	S/R	≤ 0.45	[83]
2-naphthalenesulfonate	B	1.7 – 560 000	[51]
	D	≤ 0.4	[85,86]
	D-trib	0.03 – 2.1	[85,86]
	E	≤ 20.8	[20,21]
	E-trib	62	[21]
	LC-trib	≤ 0.63	[82,84]
	R	≤ 0.63	[12,75-78,82,84]
	S/R	0.1 – 1.9	[83]
1,5-naphthalenedisulfonate	B	160 – 200 000	[51]
	D	≤ 0.38	[85,86]
	D-trib	≤ 0.17	[85]
	E	≤ 20.8	[20,21]
	E-trib	180	[21]
	LC-trib	0.09 – 3.0	[82,84]
	R	0.1 – 5.6	[12,55,74-78,80-82,84,87,88]
	S/R	0.05 – 0.53	[83]
1,6-naphthalenedisulfonate	D	≤ 0.82	[85,86]
	D-trib	≤ 0.52	[85]
	E	≤ 20	[89]
	LC-trib	0.27 – 4.3	[82,84]
	R	≤ 0.86	[75-78,81,82,84]
	S/R	0.06 – 1.8	[83]
1,7-naphthalenedisulfonate	D	0.09 – 0.22	[86]
	LC-trib	0.32 – 6.4	[82,84]
	R	≤ 0.68	[75-78,82,84]
	S/R	0.27 – 3.1	[83]

	river	concentration in µg/L[a)]	reference
2,6-naphthalenedisulfonate	B	1.3 – 250 000	[51]
	D	≤ 0.1	[85,86]
	D-trib	≤ 0.03	[85]
	E	≤ 1.4	[20,21]
	LC-trib	≤ 0.56	[82,84]
	R	≤ 0.11	[75-78,81,82,84]
	S/R	0.2 – 0.62	[83]
2,7-naphthalenedisulfonate	B	9.3 – 1 660 000	[51]
	D	≤ 0.20	[85,86]
	D-trib	≤ 0.27	[85]
	E	≤ 22	[20,21,89]
	LC-trib	0.21 – 3.1	[82,84]
	R	≤ 0.48	[74-78,82,84]
	S/R	0.14 – 1.5	[83]
1,3,5-naphthalenetrisulfonate	D	≤ 0.68	[85]
	D-trib	≤ 0.50	[85]
	R	≤ 0.07	[77,78,82,84]
	S/R	≤ 0.24	[83]
1,3,6-naphthalenetrisulfonate	D	≤ 0.11	[85]
	D-trib	≤ 0.16	[85]
	E	≤ 65.2	[20,21,89]
	LC-trib	≤ 0.85	[82,84]
	R	≤ 0.8	[75-78,82,84]
	S/R	0.15 – 2.1	[83]
1,3,7-naphthalenetrisulfonate	D	≤ 0.38	[85]
	D-trib	≤ 0.17	[85]
methylenebis-2-naphthalenesulfonate (5,5'-, 8,8'- and 5,8'-isomer)	LC-trib	0.05 – 0.48	[82,84]
	R	≤ 0.33	[22,77,78,82,84]
	S/R	0.05 – 2.5	[83]
3-hydroxy-2,7-naphthalenedisulfonate	B	1.1 – 370 000	[51]
	E	≤ 30	[20,21,89]
4-hydroxy-2,7-naphthalenedisulfonate	E	≤ 2.0	[20,21]
7-hydroxy-1,3-naphthalenedisulfonate	B	1.5 - 1 670 000	[51]
2-amino-1,5-naphthalenedisulfonate	E	≤ 20.8	[20,21]
	E-trib	940	[21]
	LC-trib	0.11 – 3.3	[82,84]
	R	≤ 4.8	[12,75-78,82,84]
	S/R	0.03 – 0.49	[83]
3-amino-1,5-naphthalenedisulfonate	E	≤ 9.8	[20]
	LC-trib	≤ 0.62	[82,84]
	R	0.97	[75-78,82,84]
	S/R	0.02 – 0.25	[83]
7-amino-1,3-naphthalenedisulfonate	B	0.2 – 76 000	[51]

	river	concentration in µg/L[a)]	reference
anthraquinonesulfonates			
2-anthraquinonesulfonate	E	≤ 7.6	[20]
1,5-anthraquinonedisulfonate	E	≤ 5.8	[89]
1,8-anthraquinonedisulfonate	R	≤ 30	[50]
	E	5.2	[89]
1-amino-4-bromo-2-anthraquinonesulfonate	E	≤ 2.0	[20]
4,4'-diamino-1,1'-bianthraquinone-3,3'-disulfonate	R	≤ 1.8	[82,84]
stilbenesulfonates			
cis-4,4'-diamino-2,2'-stilbenedisulfonate	R	≤ 1.5	[74,77]
cis-4,4'-dinitro-2,2'-stilbenedisulfonate	R	≤ 9.2	[49,55,74-78,90]
	E	≤ 6.3	[20,89]
other sulfonates			
2-hydroxy-4,6-bis(4-sulfanilo)-1,3,5-triazine	R	≤ 0.93	[75,78,82,84]

a)	The concentrations given as "≤ value" indicate that there were values reported above the detection/determination limits given in the corresponding papers and the highest value is reported in the table.
b)	Average value; number of measurements in brackets
B	Bormida river (N.W. Italy)
E	Elbe river
E-trib	Elbe tributary
D	Danube river
D-trib	Danube tributary
LC-trib	Lake Constance tributaries
M	Main river
R	Rhine river
S/R	Schwarzbach and Rodau rivers (Rhine-Main area)

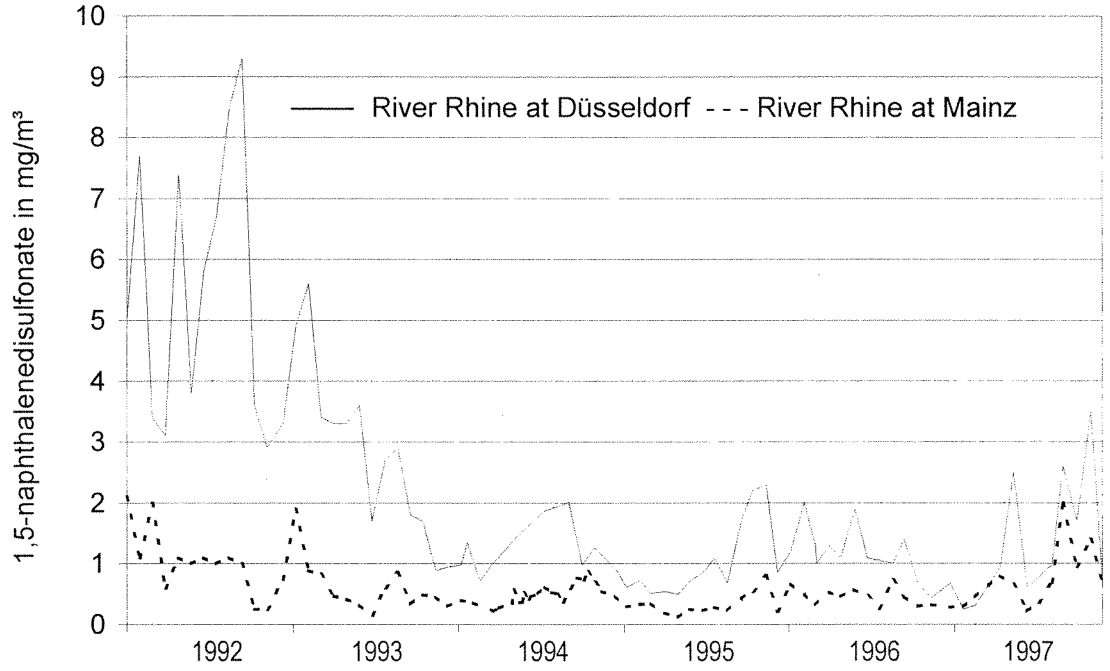

Figure 5-1: 1,5 naphthalenedisulfonate in the Rhine river at Düsseldorf and Mainz

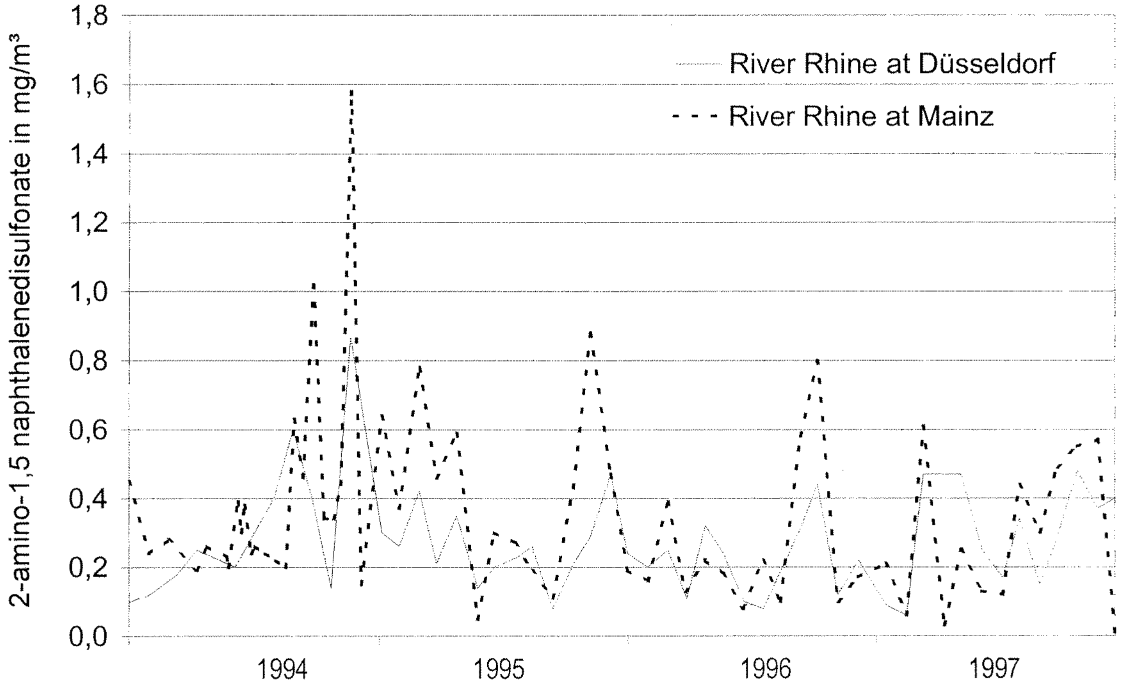

Figure 5-2: 2-amino-1,5-naphthalenedisulfonate in the Rhine river at Düsseldorf and Mainz

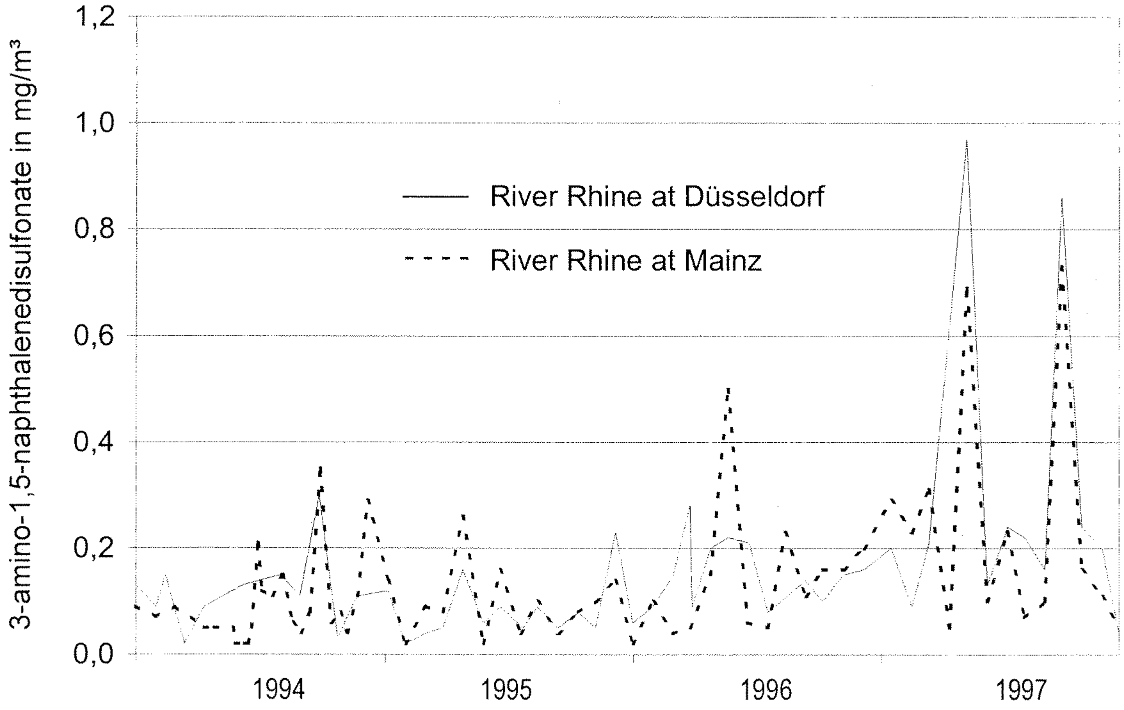

Figure 5-2: 3-amino-1,5-naphthalenedisulfonate in the Rhine river at Düsseldorf and Mainz

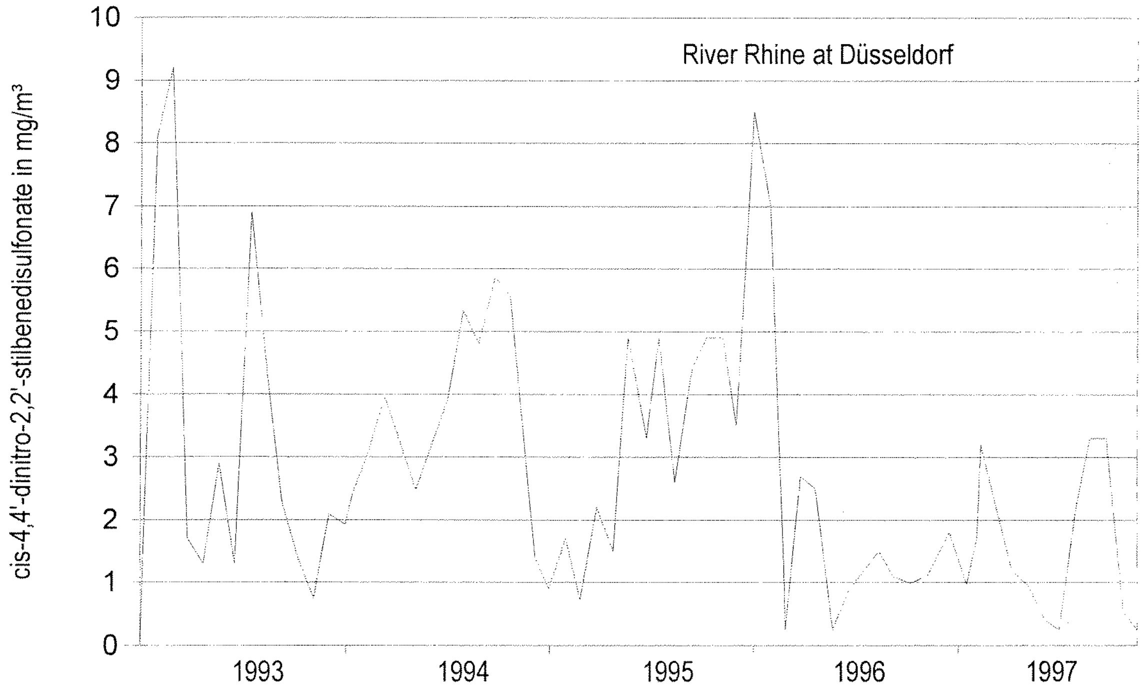

Figure 5-4: cis-4,4'-dinitro-2,2'-stilbenesulfonate in the Rhine river at Düsseldorf

5.4 Occurrence of polar aromatic sulfonates in bankside filtered water

13 PAS have been identified in bankside filtered waters of different water works along the Rhine [91], the Elbe [21] and the Danube river at Budapest [85]. Most of the sulfonated compounds, which occurred in the wells of the water works investigated are naphthalenemono-, -di-, and -trisulfonates, amino- and hydroxynaphthalenedisulfonates, cis-4,4'-dinitro-2,2'-stilbenedisulfonate, and 2-hydroxy-4,6-bis(4-sulfoanilo)-1,3,5-triazine.

These findings reflect the high production volumes, the mobility and the recalcitrant nature of these compounds. The very persistence of multiple sulfonated/substituted PAS are in good agreement with degradation studies (see subchapter 2.6) and with studies on their behavior in sewage treatment (see subchapter 5.1). Examples are 1,5NDS, 1,3,6NTS, 4,4'-dinitro-2,2'-stilbenedisulfonate and several amino- and hydroxynaphthalenedisulfonates.

Table 5-5: Polar aromatic sulfonates in bank filtered water

compound	**water**	**concentration in µg/L** a)	**reference**
naphthalenesulfonates			
2-naphthalenesulfonate	DB	≤ 0.05	[85]
	EB	≤ 0.2 (8) b)	[21]
1,5-naphthalenedisulfonate	DB	≤ 0.02	[85]
	EB	1.1 (14) - 2.5 (9) b)	[21]
	RB	0.1 – 1.3	[55,81]
1,6-naphthalenedisulfonate	DB	≤ 0.82	[85]
	RB	0.02 – 0.07	[81]
2,7-naphthalenedisulfonate	DB	≤ 0.08	[85]
	EB	≤ 2.9 (16) b)	[21]
1,3,5-naphthalenetrisulfonate	DB	≤ 0.06	[85]
1,3,6-naphthalenetrisulfonate	EB	2.4 (9) - 6.6 (10) b)	[21]
1,3,7-naphthalenetrisulfonate	DB	≤ 0.20	[85]
2-amino-1,5-naphthalenedisulfonate	RB	0.03 - 0.23	[81]
3-amino-1,5-naphthalenedisulfonate	EB	0.7 (9) - 2.5 (10) b)	[21]
	RB	0.02 - 0.13	[81]
3-hydroxy-2,7-naphthalenedisulfonate	EB	≤ 4.6 (9) b)	[21]
4-hydroxy-2,7-naphthalenedisulfonate	EB	≤ 1.7 (10) b)	[21]
stilbenesulfonates			
cis-4,4'-dinitro-2,2'-stilbenedisulfonate	RB	0.57 - 5.82	[55,81]
other sulfonates			
2-Hydroxy-4,6-bis(4-sulfanilo)-1,3,5-triazine	RB	0.53 - 0.71	[81]

a) The concentrations given as "≤ value" indicate that there were values reported above the detection/determination limits given in the corresponding papers and the highest value is reported in the table.

b) average value; number of measurements in brackets

bd	below detection/determination limit
DB	Danube river bankside filtered water
EB	Elbe river bankside filtered water
RB	Rhine river bankside filtered water

5.5 Occurrence of polar aromatic sulfonates in drinking water

The total number of published investigations on PAS determinations in drinking water is low. The PAS which have been identified in drinking water are given in Table 5-6. All these compounds belong to the class of naphthalenesulfonates. 1,5NDS and 1,3,6NTS appeared in the highest concentrations between 1 and 2 µg/L.

Neitzel found 1,5NDS and 1,3,6NTS in several drinking waters, which are made from Elbe river water. The same compounds were also identified in drinking water in further measurements for water works [22]. However, the quantitative results of a number of determinations from contract work are not yet published.

From the few published data, it could be expected that there are even more PAS traces in drinking water.

Table 5-6: Polar aromatic sulfonates in drinking water

compound	water	concentration in µg/L	reference
2-naphthalenesulfonate	DD	0.008 – 0.2	[85]
1,5-naphthalenedisulfonate	DD	bd - 0.08	[85]
	ED	0,3 - 1.5	[21]
	RD	≈ 1	[80]
1,6-naphthalenedisulfonate	DD	bd - 0.11	[85]
2,7-naphthalenedisulfonate	DD	bd - 0.08	[85]
1,3,5-naphthalenetrisulfonate	DD	bd - 0.06	[85]
1,3,6-naphthalenetrisulfonate	DD	bd - 0.11	[85]
	ED	0,6 - 2.0	[21]
1,3,7-naphthalenetrisulfonate	DD	bd - 0.81	[85]

bd	below detection/determination limit
DD	drinking water prepared from Danube river water
ED	drinking water prepared from Elbe river water
RD	drinking water prepared from Rhine river water

5.6 Conclusions

PAS have been identified in all types of investigated waters so far, including landfill leachates, sewages, river waters, bankside filtered waters and drinking waters. The number of identified compounds and their concentrations decrease from surface to drinking water. There is a larger number of data available for river waters and sewages. There are no data for lakes and for groundwater and only few data on landfill leachates and drinking water. Only naphthalenesulfonates have been found in drinking water. No systematic investigation was carried out on solids. Further measurements on ground and drinking waters as well as on sewage sludges, sediments, suspended solids and soil are recommended.

6 Behavior of polar aromatic sulfonates in drinking water treatment

Besides the bankside filtration, which is applied by a number of surface water processing water works, publications are available on the elimination of PAS from water by ozone treatment and activated carbon filtration. Reports on the behavior of PAS in other water purification processes usually used in water works have not been found in this study.

6.1 Elimination of polar aromatic sulfonates by ozone treatment

Brauch and Lange [90], Lange et al. [81], and Kühn and Baldauf [91] reported field studies on the elimination of 1,5NDS and cis-4,4'-dinitro-2,2'-stilbenedisulfonate by ozone treatment in waterworks.

In a two-step ozone treatment of a waterworks treating surface water with an ozone dose of 0.7 mg/L in the first step and 1.0 mg/L in the second step about 40-50% and 10-20% of 1,5NDS remained unchanged after the first and second step, respectively (Fig. 6-1) [81]. However, between the first and second step there was also a flocculation/sedimentation step to remove the more polar oxidation products.

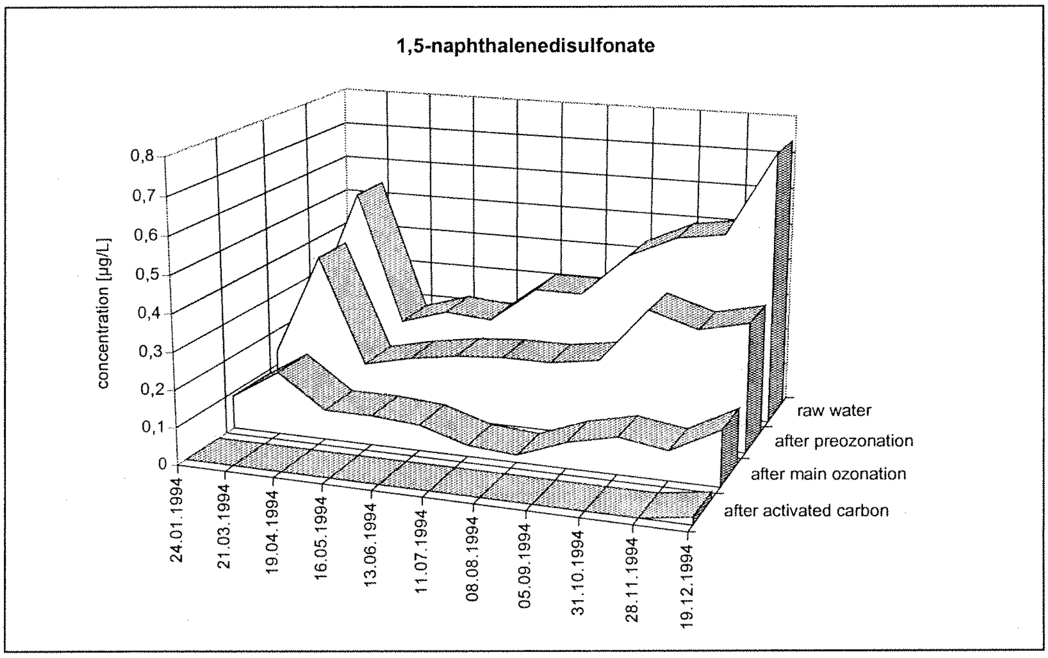

Figure 6-1: Breakthrough behavior of 1,5-napthalenedisulfonate in a water works, in which a two step ozone treatment is applied; ozone dose: 0.7 mg L^{-1} (preozonation), 1 mg L^{-1} (main ozonation); ozonation time: 4 min (preozonation), 25 min (main ozonation); pH ca. 8; DOC ca. 3.4 mg L^{-1}, according to [81].

In another waterworks using river bank filtrate as raw water about 80% of cis-4,4'-dinitro-2,2'-stilbenedisulfonate was removed by a one-step ozone treatment [81].

The primary reaction of ozone with 1,5NDS, 2-amino-5-chloro-4-methylbenzenesulfonate, anthraquinone-2,6-disulfonate, cis-4,4'-dinitro-2,2'-stilbenedisulfonate, and

3-amino-1,5-naphthalenedisulfonate was studied in bench-scale experiments [92] with sulfonate concentrations between 5 and 100 µg/L and ozone doses of about 1 mg/L.

In these experiments the influence of ozone dose, initial sulfonate concentration, pH, hydrogen carbonate content, and DOC on the reaction of ozone with 1,5NDS was studied. Even in deionized water, where there is only little concurrence with the natural organic compounds (DOC ≈ 0.2 mg/L) 1,5NDS was oxidized incompletely. Using an initial ozone concentration of 0.7 mg/L 15% of 1,5NDS was recovered after a reaction time of 45 min. In most of the water works the reaction times are shorter than 45 min and the DOC values higher than 1 mg/L. Thus, the trace concentrations of 1,5NDS after ozonation are in general 40-60% of the raw water value [81].

With an initial concentration of cis-4,4'-dinitro-2,2-stilbenedisulfonate of 5 µg/L and an ozone dose of about 1 mg/L after 10 min about 10% of this compound remained unchanged. The elimination was complete after 30 min. The concentration of the other tested compounds dropped below the detection limit already after 2 min [92].

By-products from oxidation of PAS by ozone have not been identified in these investigations.

6.2 Elimination of polar aromatic sulfonates by activated carbon adsorption

Field studies in water works were reported by Brauch and Lange [90], Lange et al. [81], and Kühn and Baldauf [91]. It turned out that the elimination efficiency strongly depends on the process conditions in the different water works.

In a water works, where the treatment consists of three main steps, i.e. iron removal, manganese removal and a final filtration step by two parallel granular activated carbon (GAC) adsorbers, the polar naphthalenesulfonates could not always be efficiently removed (s. figure 6-2).

The naphthalenesulfonates, which remained in the water after iron and manganese removal, showed an early breakthrough on GAC [81]. At loads larger than 35 m^3 of water per kg of GAC the breakthrough of 1,5NDS at a concentration of 0.6 µg/L was complete [91].

In another water works, where a larger part of the sulfonates is eliminated by ozone treatment and flocculation/sedimentation before entering the charcoal filters, a nearly quantitative removal was observed for 1,5NDS, see figure 6-1 [81].

Data from a water works with ozone-biological active charcoal filtration indicate almost complete removal of PAS with low concentrations (≤ 0.1 µg/L) of 1,5NDS and 1,3,5-/1,3,6NTS in drinking water[4].

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[4] H. Smeenk: private communication

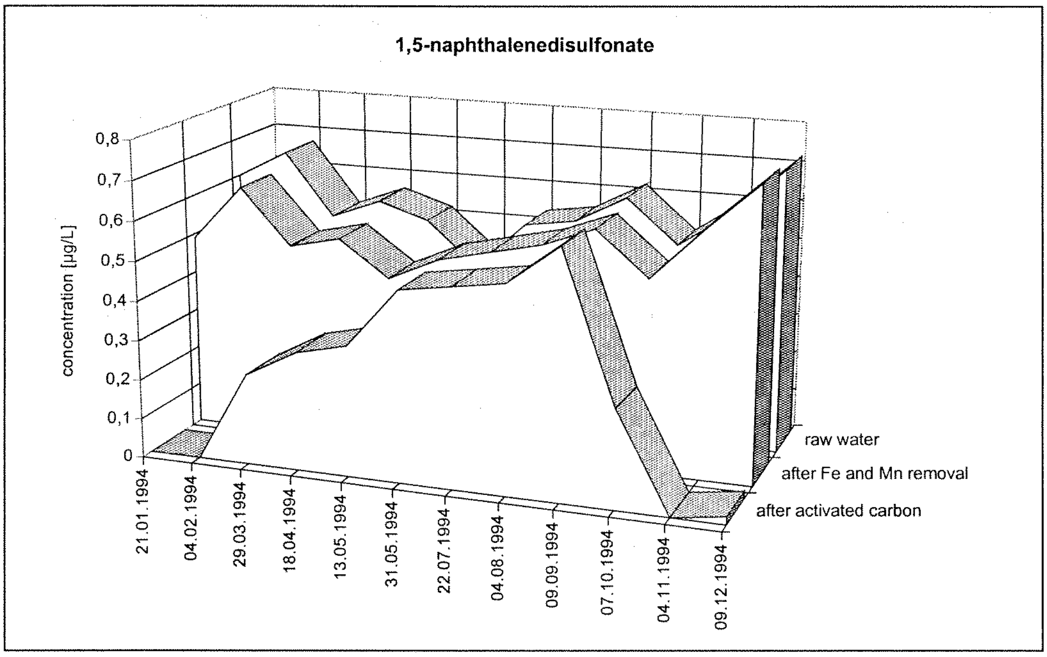

Figure 6-2: Breakthrough behavior of 1,5-naphthalenedisulfonate in water works 1. Two parallel filters, each containing 50 m^3 activated carbon; running time and load of the activated carbon filters: filter 1: 15.12.1993–27.09.1994 (1 240 220 m^3), filter 2: 15.06.1993 – 11.10.1994 (1 648 160 m^3), reproduced from [81].

Laboratory investigations on the adsorption of PAS on activated carbon are reported by Schullerer [93], Johannsen et al. [94,95], Bastian et al. [69], Fichtner et al. [20], Ulmer [96], and Neitzel et al. [21]. Schullerer [93] and Johannsen et al. [94] observed a concentration dependent adsorption equilibrium, which is unusual for adsorption experiments with single compounds. The latter authors [94] tried to explain this effect in terms of associate formation of the sulfonates.

Thermodynamic and kinetic aspects of the adsorption of ten selected PAS on activated carbon were investigated experimentally and via modeling by Ulmer [96]. By means of single component adsorption isotherms he found - like Schullerer [93] and Johannsen et al. [94] - unusual concentration dependent adsorption/desorption equilibria. For multiple sulfonated compounds, e.g. 1,5NDS and 1,3,5NTS, the adsorption ability strongly decreased with increasing initial sulfonate concentrations. He further observed a significant pH increase during the equilibration, which was discussed as ion-exchange process taking place on the surface of the charcoal. For the determination of the Freundlich parameters used for modeling, the pH was kept constant during equilibration, which avoided a concentration dependence.

The modeling on the basis of the so-called Polanyi potential theory leads to the conclusion that the adsorption of small monosulfonated aromatics on activated carbon is mainly determined by van-der-Waals interaction between sorptive and sorbens. Further model calculations and experimental investigations on the pH dependent adsorption behavior of PAS suggested again the dominance of van-der-Waals interaction for the monosulfonates. For higher sulfonated compounds a decrease of the sulfonate load on activated carbon was observed.

Ulmer [96] also determined diffusion coefficients of the selected PAS on activated carbon and found no concentration dependence up to an initial sulfonate concentration of 1 mmol/L. The diffusion coefficients decreased linear with the molar mass of the sulfonates. In similar diffusion experiments with the so-called rapid small scale column set-up Johannsen [95] evaluated decreasing diffusion coefficients with increasing sulfonate concentration.

The breakthrough behavior of five selected PAS was studied in a pilot-scale activated carbon filter using a natural ground water (DOC = 1,9 µg/L) spiked with these sulfonates at a level of 10 µg/L [96]. For the monosulfonates 1NS and 2-anthraquinonesulfonate no conclusions could be drawn from this experiment due to interfering biodegradation of 1NS and nearly irreversible adsorption of 2-anthraquinonesulfonate. In a filter depth of 60 cm 50% breakthrough occurred for 1,3,6NTS after a specific throughput of about 50 m^3/kg, after 70 m^3/kg for 1,5NDS and 200 m^3 for 3-nitrobenzenesulfonate.

Fichtner et al. [20] used 20 mg/L of activated carbon F300 (Chemviron Carbon, Brussels, Belgium) for shaking biologically pretreated Elbe river water for 24 h in a closed bottle. Due to their high polarity,1,5NDS and 1,3,6NTS could not be adsorbed completely on the activated carbon. After biological treatment in a test-filter, where 15% of 1,5NDS was removed, and after activated carbon adsorption still 50% to 70% of this substance remained in the water.

Neitzel et al. [21] carried out adsorption experiments similar to the experiments of Fichtner et al. [20] using a solution of PAS in Elbe water with initial sulfonate concentrations between 49 µg/L and 140 µg/L and activated carbon F300 (Chemviron Carbon GmbH; particle size: 0.4 - 0.6 mm) in concentrations between 5 mg/L and 300 mg/L. At a practically relevant activated carbon concentration of 20 mg/L they estimated sulfonate residues in the aqueous phase between 70% and 80% for the two-fold sulfonated compounds and 60% for the monosulfonates.

Similar shaking experiments with Chemviron F300 activated carbon were carried out by Bastian et al. [69] on aqueous solutions with one or several PAS at an initial concentration of 10 mg/L. In agreement with the other authors they found a good adsorption ability for monosulfonates, which is comparable to other aromatic compounds, and a decreased adsorption ability for disulfonates.

6.3 Conclusions

Field and laboratory work on the elimination of PAS during drinking water treatment suggest that a multibarrier approach is needed in order to remove PAS traces of about 1 µg/L down to concentrations below the analytical detection limits, which are of the order 0.1 µg/L. From the limited amount of data 1,5NDS and 1,3,6NTS seem to be relevant for drinking water. Collection of more data on drinking water is recommended. Only Oxidation by ozone or charcoal adsorption is not effective enough. Combination of ozone treatment with an adsorption step using frequently reactivated/exchanged activated charcoal is suited for that purpose. As a final risk assessment for PAS is not possible at present, and the treatment plants are not optimized for PAS elimination, PAS immissions into the raw waters should be reduced rather than adapting the water treatment processes.

7 Appendix: Sulfonated compounds and mixtures of compounds included in the OECD HPVC List

The HPVC list contains those chemicals which are produced or imported at levels greater than 1,000 tonnes per year in at least one Member country.

It has been compiled based upon submissions from 20 Member countries and by combining the European Union's HPV list according to EC Regulation 793/93, and is used by Member countries in choosing chemicals on which to make an initial assessment of their potential to exert a risk to man or the environment.

These initial assessments, which are a fundamental part of the OECD Existing Chemicals Programme, are based on a relatively restricted set of data elements, the Screening Information Data Set or SIDS. The intention is to screen chemicals for potential risk, so that resources can be concentrated on undertaking further work on chemicals of concern.

Using the data from the SIDS, mainly provided by cooperation with the chemical industry, Member countries prepare a SIDS Initial Assessment Report, SIAR, which highlights any potential risk and contains recommendations for further action, if any, on the chemical.

The SIAR is discussed at a meeting of experts from all Member countries, from other international organisations, and from non-Member countries, as nominated by the United Nations' International Programme on Chemical Safety (IPCS), as well as representatives of the manufacturing companies. The SIAR, amended as appropriate, is made available world-wide by publication through the United Nations Environment Programme (UNEP) Chemicals.

In the attached extract of the 1997 OECD List of High Production Volume Chemicals, the various columns are indicated by:

CAS-No.	which gives the Chemicals Abstract Registry Number;
SIDS	which indicates those chemicals in the OECD SIDS programme;
Chemical Name	which gives the name of the chemical, abbreviated as necessary to 80 characters
SIDS data probable	means that a computerised research for readily available information showed that there are probably SIDS data gaps to be filled;
ICSC	refers to the availability and number of International Chemical Safety Cards produced by IPCS.
EHC	refers to the availability and number of IPCS Environmental Health Criteria documents and

Highlighted compounds or components of technical mixtures have been identified in the aquatic environment.

CAS-No.	SIDS	Chemical Name	No of EXICHEM entries	SIDS data gap probable	ICSC	EHC
80-51-3		Benzenesulfonic acid, 4,4'-oxybis-, dihydrazide	1			
81-04-9		**Naphthalene-1,5-disulphonic acid**	**1**			
81-11-8	**SIDS**	**4,4'-Diaminostilbene-2,2'-disulfonic acid**	**4**	**yes**		
81-16-3		2-Aminonaphthalene-1-sulphonic acid	7	yes		
87-02-5		2-Naphthalenesulfonic acid, 7-amino-4-hydroxy-	7			
88-44-8		m-Toluenesulfonic acid, 6-amino-	8			
88-51-7		m-Toluenesulfonate, 6-amino-4-chloro				
88-53-9		**5-Amino-2-chlorotoluene-4-sulphonic acid**	**5**			
90-51-7		2-Naphthsulfonate, 6-amino-4-hydroxy	4			
98-11-3		Benzenesulfonic acid	2	yes		
104-15-4		**p-Toluenesulfonic acid**	**5**	**yes**	**773**	
116-81-4		**2-Anthracenesulfonic acid, 1-amino-4-bromo-**	**1**			
118-33-2		1,3-Naphthalenedisulfonic acid, 6-amino-	2			
120-18-3		**Naphthalene-2-sulphonic acid**	**1**			
121-03-9	**SIDS**	**o-Toluenesulfonic acid, 5-nitro-**	**4**	**yes**		
121-47-1		**3-Aminobenzenesulphonic acid**	**3**			
121-57-3		**Benzenesulfonic acid, 4-amino-**	**4**	**yes**	**569**	
127-68-4		**Sodium m-nitrobenzenesulfonate**	**6**	**yes**		
657-84-1		**Sodium-p-toluenesulfonate**		**yes**		
825-90-1		**Benzenesulfonic acid, 4-hydroxy-, monosodium salt**				
833-66-9		Potassium 6-hydroxynaphthalene-2-sulphonate	1			
842-18-2		**Dipotassium 7-hydroxynaphthalene-1,3-disulphonate**	**6**			
887-76-3		4,4'-azo-3-hydroxynaphthalene-1-sulphonate	2			
1126-34-7		**Sodium 3-aminobenzenesulfonate**	**2**			
1300-72-7		Xylenesulfonic acid, sodium salt	5	yes		
1322-98-1	SIDS	Benzenesulfonic acid, decyl, sodium salt				
1331-61-9		Benzenesulfonic acid, dodecyl-, ammonium		yes		
1333-39-7		**Benzenesulfonic acid, hydroxy-**	**2**			
1655-29-4		**Disodium 1,5-naphthalenesulfonate**	**2**			
3709-43-1		**Disodium 4,4'-dinitrostilbene-2,2'-disulphonate**	**2**			
5123-63-7		Sodium 3-diethylaminobenzenesulfonate	2			
7336-20-1		**Disodium 4,4'-diaminostilbene-2,2'-disulphonate**	**3**			
8061-51-6		Lignosulfonic acid, sodium salt	2			
8061-54-9		Lignosulfonic acid, magnesium salt				
9066-50-6		Lignosulfonic acid, chromium salt	1			
9084-06-4		Naphthalenesulfonic acid, polymer with formaldehyde, sodium	1			
11117-11-6		Calcium bis(tetrapropylenebenzenesulphonate)	1			
12068-03-0		**Benzenesulfonic acid, methyl-, sodium salt**				
13863-31-5		Benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis+5-++4-+(2-hyd				
17691-19-9		Sodium 4-chloro-3-nitrobenzenesulphonate	1			
25155-30-0	SIDS	Benzenesulfonic acid, dodecyl, sodium salt	7	yes	1189	
25167-32-2		Disodium 2,2'-oxybis-5-dodecylbenzenesulphonate	1			
25321-41-9		Xylenesulphonic acid	1			
25322-17-2		Naphthalenesulfonic acid, dinonyl-				
25496-01-9		Benzenesulfonic acid, tridecyl-	1	yes		
25619-56-1		Naphthalenesulfonic acid, dinonyl-, barium salt				
25956-17-6		2-Naphthalenesulfonic acid, 6-hydroxy-5-+(6-methoxy-4-sulfo-	1			
26248-24-8	SIDS	Benzenesulfonic acid, tridecyl-, sodium salt	1	yes		
26264-05-1		Benzenesulfonic acid, dodecyl-, isopropylamine salt				
26264-06-2		Benzenesulfonic acid, dodecyl-, calcium salt	1	yes		
26447-10-9		Xylenesulfonic acid, ammonium salt		yes		

CAS-No.	SIDS	Chemical Name	No of EXICHEM entries	SIDS data gap probable	ICSC	EHC
26545-58-4		**Sodium dinaphthyl methane disulfonate**	**2**			
27176-87-0		Benzenesulfonic acid, dodecyl-	4	yes		
27323-41-7		Benzenesulfonic acid, dodecyl-, compd. with 2,2',2"-nitrilo				
27636-75-5	SIDS	Benzenesulfonic acid, undecyl, sodium salt				
28348-53-0		**Sodium cumenesulfonate**	**2**	**yes**		
28519-02-0		Benzenesulfonic acid, dodecyl(sulfophenoxy)-, disodium salt				
28631-63-2		**2-(or 4)-(isopropyl)benzenesulphonic acid**	**1**			
28855-17-6		Octadecylbenzenesulphonic acid	1			
32073-22-6		**Cumenesulfonic acid, sodium salt**				
37475-88-0		**Benzenesulfonic acid, (1-methylethyl)-,**		**yes**		
38185-06-7		Benzenesulfonic acid, 4-chloro-3,5-dinitro-, potassium salt				
41267-43-0		1,4-Benzenedisulfonic acid, 1,3,5-triazine deriv Na salt				
61789-85-3		Sulfonic acids, petroleum				
61789-86-4		Sulfonic acids, petroleum, calcium salts	2			
61790-48-5		Sulfonic acids, petroleum, barium salts				
63589-25-3		4-Diazo-3,4-dihydro-7-nitro-3-oxonaphthal-1-sulphonic acid	2			
68081-81-2	SIDS	Benzenesulfonic acid, mono-C10-16-alkyl, sodium salts	1			169
68153-01-5		**Naphthalenesulfonic acids**	**2**			
68201-32-1		Asphalt, sulfonated, sodium salt				
68411-30-3	SIDS	Benzenesulfonic acid, C10-13-alkyl derivs., sodium salts	2			169
68411-32-5		Benzenesulfonic acid, dodecyl-, branched				
68512-34-5		Lignosulfonic acid, sodium salt, sulfomethylated				
68584-22-5		Benzenesulfonic acid, C10-16-alkyl derivatives	2			169
68608-26-4		Sulfonic acids, petroleum, sodium salts	2			
68608-88-8		Benzenesulfonic acid, mono-C11-13-branched alkyl derivs.	1			
68783-96-0		Sulfonic acids, petroleum, calcium salts, overbased	2			
68953-90-2		Benzenesulfonic acid, mono-C7-17-alkyl derivs.	1			
68953-96-8		Benzenesulfonic acid, mono-C11-13-branched alkyl derivs., ca				
70024-67-8		Benzenesulfonic acid, C16-24-alkyl derivs.	1			
70024-69-0		Benzenesulfonic acid, mono-C16-24-alkyl				
70024-72-5		Benzenesulfonic acid, mono-C19-28-alkyl derivs, calcium salt	1			
70788-37-3		**2-(or 4)-toluenesulphonic acid**	**1**			
71486-79-8		Benzenesulfonic acid, mono-C15-30-branched alkyl and di-C				
71549-79-6		Benzenesulfonic acid, mono-C15-30-branched alkyl and di-C				
71786-47-5		Benzenesulfonic acid, mono- and dialkyl derivs. Mg salts	1			
75199-12-1		Benzenesulfonic acid, 4-hydroxy-, polymer with formaldehy				
78330-12-8		Benzenesulfonic acid, mono- and di-C15-30-alkyl derivs.,				
85117-49-3		Benzenesulfonic acid, mono-C10-14-alkyl derivs.	1			
85117-50-6	SIDS	Benzenesulfonic acid, C10-14-alkyl derivs., sodium salts	1			
85536-14-7		Benzenesulfonic acid, C10-13-sec-alkyl derivatives	21			
90194-27-7		Benzenesulfonic acid, C10-60-alkyl derivs., calcium salts	1			
90194-45-9		Benzenesulfonic acid, C10-13-alkyl derivs., sodium salts	1			
90194-47-1		Benzenesulfonic acid, mono-C15-36-branched alkyl derivs.	2			
90218-04-5		Benzenesulfonic acid, C15-36-branched alkyl, sodium salts	1			
90218-34-1		Benzenesulfonic acid, C10-14-branched derivs. sodium salts	1			

CAS-No.	SIDS	Chemical Name	No of EXICHEM entries	SIDS data gap probable	ICSC	EHC
90218-44-3		Hydroxybenzenesulfonic acid, sodium salt, HCHO react prods.	1			
90268-85-2		Calcium, C15-36-branched alkylbenzenesulfonate C10-14-branch	1			
90387-57-8		Formaldehyde, prods. with sulfonated 1,1'-oxybistoluene, sod	1			
90431-56-4		Magnesium, C15-36-alkylbenzenesulfonate complexes	1			
91078-64-7		Sodium naphthosulfonate, branched and linear Bu derivs.,	2			
91078-68-1		**Naphthosulfonates, reaction prod with HCHO, sodium salts**	**1**			
91696-70-7		Benzenesulfonic acid, C14-44-branched alkyl, calcium salts	1			
91696-73-0		Benzenesulfonic acid, C14-44-br'ch & linear, calcium salts	1			
91696-74-1		Benzenesulfonic acid, C14-44-br'ch & linear, calcium salts	1			
91782-38-6		Benzenesulfonic acid, C10-60-alkyl derivs.	1			
93028-29-6		Benzenesulfonic acid, C10-60-alkyl derivs., magnesium salts	1			
93820-57-6		Benzenesulfonic acid, di-C10-18-alkyl, calcium salts	1			
93924-63-1		**Naphthalenesulfonic acids, prod with HCHO, ammonium salts**	**1**			
93924-64-2		**Naphthalenesulfonic acids, prods with HCHO, sodium salts**	**1**			
93965-02-7		Benzenesulfonic acid, 2,2'-(1,2-ethenedi	2			
115733-09-0		Benzenesulfonic acid, C14-24-branched and linear alkyl de				
115733-10-3		Benzenesulfonic acid, C14-24-branched & linear Ca salts	1			
115829-36-2		Benzenesulfonic acid, C14-24-branched and linear alkyl deriv	1			
119345-03-8		Benzene, 1,1'-oxybis-, tetrapropylene derivs., sulfonated				
119345-04-9		Benzene, 1,1'-oxybis-, tetrapropylene derivs., sulfonated				

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Colophon

Publisher	Association of River Waterworks - RIWA
Cover and printing	B.V. Drukkerij De Eendracht, Schiedam

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