

Chapter 2

Organic Contaminants from Industrial Wastewaters: Identification, Toxicity and Fate in the Environment

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Abstract Industrialization and urbanization in the industrial nations and increasingly also in emerging and developing nations have led to an intensive and still increasing use of freshwater resources. Industries are one of the most important pollution sources and the discharged wastewaters may contain very diverse organic compound groups. Among those, lipophilic contaminants possessing functional groups which are not common in nature rank among the compounds which are most persistent. There have been strong efforts in environmental sciences for a comprehensive

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characterization of chemical contamination and the related impacts, in order to provide data as a basis for management measures. Here we review the current state of knowledge about organic contaminants from industrial sources. We present information about (i) the identification of organic contaminants in industrial wastewaters, (ii) how these compounds are traced in aquatic systems, and (iii) on their toxicity for aquatic organisms as observed in laboratory experiments and in the field.

Major advancements concerning this theme include the development of new analytical techniques which allow for the identification of previously unknown, emerging contaminants. Overall, these studies proved the heterogeneity of the chemical composition of industrial wastewaters, even from the same industry branches. The observed differences are related to different industrial production processes, leading to the presence of varying synthesis educts, additives, products and byproducts in the wastewaters, of which many might occur in the environment but have not yet been identified. Attempts which were made to trace industrial discharges in aquatic systems proved accordingly the presence of very heterogenic organic contaminant mixtures in the environment. We therefore conclude that our knowledge about the chemical composition of industrial wastewaters and about the occurrence of industrial organic contaminants in the environment is as yet very limited.

A further advancement was the development of a combination of chemical and toxicological methods to identify causative organic constituents including emerging contaminants which contribute to the toxicity of industrial wastewaters. Only a few studies in this field are available, although the results obtained so far are promising. Several studies demonstrated the toxic activity of field samples and relate the observed effects to the presence of industrial organic contaminants. Exposure experiments in the field proved the bioaccumulation of specific industrial contaminants and assessed the associated toxic effects. The effects of chemical contamination on aquatic invertebrate communities was shown in field studies combining chemical and biological methods, although industrial inputs were not disentangled from other pollution sources. Ecological surveys of sites contaminated by industrial point sources combined with a comprehensive chemical characterization and toxicity evaluation are missing.

Some of the identified organic contaminants are related to characteristic industrial production processes and their presence in water, sediment or biota therefore indicates the input of specific industrial wastewaters. Accordingly, these compounds can be used as industrial markers. As synthesis of the reviewed information we present a list of potential industrial marker compounds. We suggest the proceeding application of the marker concept which helps to verify the input of specific industrial wastewaters to aquatic systems and to investigate the spatial distribution of the emission. Such information is useful to disentangle different emission sources for the subsequent investigation of their potential impacts in the environment. We present further research strategies which are in our opinion promising to address the identified gaps in knowledge.

Keywords Emerging contaminants • Industrial chemicals • Industrial pollution • Organic markers • Toxicity-based fractionation • Aquatic systems • Aquatic organisms

List of Abbreviations

CAS No.	Unique identifier of a chemical, assigned by the Chemical Abstracts Service
CPE	Chlorophenylethanol
DCPE	Chlorophenylethanoldichloroethanol
DBP	Dichlorobenzophenone
DDA	Bis(chlorophenyl)acetic acid
DDABE	Bis(chlorophenyl)acetic acid butylester
DDAMA	Bis(chlorophenyl)acetic acid methylamide
DDCN	Bis(chlorophenyl)acetonitrile
DDD	Bis(chlorophenyl)dichloroethane
DDE	Bis(chlorophenyl)dichloroethene
DDMU	Bis(chlorophenyl)chloroethene
DDT	Bis(chlorophenyl)trichloroethane
DOC	Dissolved organic carbon
DTPA	Diethylenetriaminepentaacetic acid
EC ₅₀	Concentration of a chemical which induces a defined response of 50 % of the members of a tested population after a specified test duration
EDTA	Ethylenediaminetetraacetic acid
FIA-MS-MS	Flow injection analysis-tandem mass spectrometry
GC/MS	Gas chromatography-mass spectrometry
HCB	Hexachlorobenzene
HCHs	Hexachlorocyclohexanes
HPLC	High performance liquid chromatography
HPLC-ED	High performance liquid chromatography with electrochemical detection
HT-GC/MS	High temperature-gas chromatography-mass spectrometry
IPC-ESI-MS	Ion-pair chromatography/electrospray-mass spectrometry
LAS	Linear alkylbenzene sulfonates
LC ₅₀	Concentration of a chemical required to kill 50 % of the members of a tested population after a specified test duration
LC/ESI-MS ⁿ	Liquid chromatography-electrospray ionization/multi-stage mass spectrometry
LC/MS	Liquid chromatography-mass spectrometry
LC/MS-MS	Liquid chromatography tandem mass spectrometry
LC/UV	Liquid chromatography with UV detection
MCPE	Chlorophenylchloroethanol
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo- <i>p</i> -dioxins
PCDFs	Polychlorinated dibenzofurans
PeBDE	Pentabromodiphenyl ether

POCIS	Polar organic chemical integrative sampler
SPE	Solid phase extraction
SPME	Solid phase microextraction
TLC	Thin layer chromatography
UNEP	United Nations Environment Programme

2.1 Introduction

Chemical contamination was defined as a problem with global relevance, one of nine “planetary boundaries”, which should not be transgressed in order to avoid unacceptable global changes (Rockström et al. 2009). In a report on worldwide toxic contamination problems and their implications for human health, mining and industrial activities accounted for nearly all of the documented issues (Blacksmith Institute and Green Cross Switzerland 2011). Overall, industrialization and urbanization in the industrial nations and increasingly also in emerging and developing nations have led to an intensive and still increasing use of water resources (Fig. 2.1). The involved chemical contamination led to a deterioration of rivers, lakes and



Fig. 2.1 Industrial complex in South India, where a tire and rubber production unit, a paper mill, tanneries and chemical production sites discharge the produced wastewaters into public waterways (Photo: Tim Jennerjahn)

coastal waters in many areas. In the industrial nations, these problems were partially solved by source control and by the implementation of technical systems such as sewage treatment. However, there still remain major challenges. The foresight report of the UNEP lists degradation of inland waters in developing nations due to the discharge of untreated wastewaters as one of the 21 most important environmental problems of the twenty-first century (UNEP 2012).

Industries are one of the most important sources for the contamination of aquatic systems. The quantitative composition of the wastewater constituents and their chemical characteristics differ according to the type of the operating production processes. Many organic contaminants are solely discharged by industries which apply certain production processes. Accordingly, high concentrations of such characteristic compounds are only detectable in areas where the related industries are located. Symptomatic are also the high but largely varying concentrations in the wastewaters and the simultaneous occurrence of a large number of chemically heterogeneous compounds. A distinct analytical characterization is often hindered due to the large variability of the wastewater quality caused by the discontinuity of many production processes.

The variety of organic compounds which is industrially synthesized is immense. For example, the European Inventory of Existing Commercial Chemical Substances lists about 100,000 synthesized chemicals which were deemed to be on the European Community market in the period 1971–1981. The list is counting for about 99 % of the chemicals' volume on the market. About 30,000–70,000 of the listed chemicals are used on a daily basis (European Inventory of Existing Chemical Substances, Schwarzenbach et al. 2006). The number of byproducts, educts and intermediates though, which might be performed during the synthesis of these regularly used chemicals, is unknown.

The wastewater constituents are discharged into aquatic systems in their dissolved form, associated with colloids or attached to particulate matter. Depending on their physico-chemical properties and the environmental conditions, they undergo different processes after discharge, which include partitioning between phases, transport and/or degradation. A dynamic partitioning is occurring between the following phases: water and atmosphere, water and particulate matter, water and biota as well as particulate matter and biota. Lipophilic organic compounds tend to be bound to particulate matter, so that sediments can be considered as pollution reservoirs (e.g. Baumard et al. 1998). Transport can happen within the dissolved or the particulate phase, sometimes over long distances. This is particularly true for persistent organic pollutants such as DDT, PCDDs/PCDFs and heptachlor.

In the aquatic system, biotic and/or abiotic degradation processes lead to the transformation of organic contaminants to metabolites or to their complete mineralization to H_2O and CO_2 . Most organic contaminants – even persistent ones – are degradable under favorable conditions, the latter though within long time periods. The degradation processes depend strongly on the physico-chemical properties of the compounds, e.g. the water solubility. Water soluble organic compounds are often more rapidly degraded than lipophilic compounds (e.g. Berndt 1996).

Dissolved aliphatic alcohols and carboxylic acids were smoothly degraded in an anaerobic milieu, whereas the degradation of the same compound classes with ether bounds or branched hydrocarbon chains took much longer (Kameya et al. 1995). From this it follows that particularly lipophilic organic compounds, possessing functional groups which are not common in nature, rank among the most persistent compounds.

Aquatic biota accumulates particularly such persistent, lipophilic organic contaminants and biomagnification in aquatic food webs has been documented for selected priority pollutants such as HCB, PCBs, PeBDE, dieldrin and mirex (Kelly et al. 2007). The toxicities of several contaminant groups were tested with experimental aquatic species and revealed sublethal to acute toxicity of different parent PAHs, organochlorine pesticides and tributyltin amongst others (e.g. Matthiessen and Law 2002; Thompson et al. 2007). Organic contaminants may have an impact on molecular and cellular processes and also induce changes on the organism, population and community level, which was shown for the antifouling agent tributyltin (Warwick et al. 1990; Fent 2007; Matthiessen and Law 2002). The endocrine disrupting property of this compound has been shown to cause imposex in gastropods (Harding et al. 1999) and to affect not just coastal mollusk populations but also cause reductions in species diversity in coastal invertebrate communities (e.g. Matthiessen and Law 2002). Responses to contaminants are species-specific and help the organisms to cope under various stressors, leading to their acclimation or adaptation to environmental conditions. Sensitive species with a low ability to respond to changes are particularly threatened.

A decline of species holding important ecological functions may negatively affect the whole ecosystem. Many fish and macrobenthic invertebrate species are furthermore exploited as fisheries resources. A reduction of economically important species can therefore cause an impairment of local economies and livelihoods. The contamination of economically important species is moreover posing a threat to the health of humans, as consumers of fish, mussels and crabs.

Accordingly, there have been strong efforts in environmental sciences for a comprehensive characterization of chemical contamination and the related impacts, in order to provide data as a basis for management measures. We present here a comprehensive review of the current state of knowledge about organic contaminants from industrial sources. We present information about (i) the identification of organic contaminants in industrial wastewaters, (ii) how they are traced in aquatic systems, and (iii) their toxicity for aquatic organisms as observed in laboratory experiments and in the field.

Standard search machines were used to find relevant peer reviewed literature from the period 1970–2012. For Table 2.1 also data from two Ph.D. theses and from one report were cited due to the limited available information. Unspecific keywords were used for the literature search such as “industrial wastewaters” and “industrial effluents” in combination with “organic pollutants” and “organic contaminants”. From the several 100 matches found with this method, only studies which focus on the identification and chemical/toxicological characterization of low-molecular

weight organic compounds in industrial wastewaters and impacted aquatic systems were selected. Studies which focus on treatment techniques, remediation or on bulk parameters to study industrial contamination were neglected. Furthermore, only field studies were considered in which the detected contaminants were unequivocally attributed to industrial sources.

2.2 Chemical Characterization of Industrial Wastewaters

2.2.1 *Analytical Approaches for the Identification of Organic Contaminants in Industrial Wastewaters*

Improvements in the chemical characterization of industrial effluents are closely linked with the development of appropriate analytical tools. A thorough overview on analytical methods used to characterize complex contaminant mixtures in industrial wastewaters has been given by Castillo and Barceló (1999a). More general reviews not only focusing on industrial but also on municipal effluents have recently been given by Sanchez Rojas and Bosch Ojeda (2005) as well as by Giger (2009). The later compilation described the advances in the detection of polar and amphiphilic contaminants as important constituents in wastewater. A more specific review summarized the application of LC/MS for the analysis of endocrine disrupting agents in wastewater partially considering also industrial effluents (Postigo et al. 2009).

Noteworthy, the enormous contributions of GC/MS and LC/MS techniques with respect to the identification and quantification of organic constituents in different types of industrial wastewater have been summarized in all three reviews. These techniques are responsible for the most important progress in the analytical detection of industrial contaminants, hence nearly all recent studies (reported in this review) are based analytically on well established GC/MS and LC/MS methods.

Recently, only very few studies reported the application of new analytical methods. Some reports represent slight modifications of standard techniques. E.g. Castillo et al. (1999b) reported on the extension of the GC/MS towards higher gas chromatographic temperature (HT-GC/MS) to detect higher boiling substances in industrial effluents. Further studies focused on optimization of sample treatment and extraction procedures. These approaches include sequential solid phase extraction (SSPE) or novel passive sampling devices such as POCIS (Castillo et al. 1999b; Alvarez et al. 2005). Lastly, some publications described the optimization of specific analytical methods for the detection of preselected industrial contaminants. Rodriguez et al. (2004) followed 2-mercaptobenzothiazol in tannery wastewater by liquid chromatography coupled to an amperometric detector. Schriks et al. (2010) quantified glucocorticoids in wastewater using high resolution mass spectrometry.

2.2.2 *Organic Contaminants Which Have Been Identified in Different Types of Industrial Wastewaters*

Since the 1970s, mainly wastewaters from the textile industry, tanneries, the petrochemical industry, pulp and paper industry, rubber and tire production and from chemical production sites were investigated. The studies were almost exclusively conducted in industrial nations of the northern hemisphere, i.e. Europe, the United States and Japan. Although during the last two decades industrial production sites were more and more shifted to newly industrialized countries, such as China, India and Brazil, studies from these countries are lacking.

In most cases, the effluents were investigated, after treatment and before release to the environment. The sort of applied methods confine the spectrum of identifiable compounds. Using purge techniques or head space SPME for sample preparation (Smith 1990; James and Stack 1997; López-Grimau et al. 2006), only volatile organic compounds were extracted from the sample matrix. A compound separation with liquid chromatography and subsequent application of mass spectrometry (e.g. Castillo and Barceló 2001; Loos et al. 2007; Schriks et al. 2010) allows for the detection of hydrophilic and amphiphilic compounds. Analyses with GC/MS are relevant for the determination of volatile and semivolatile lipophilic organic compounds. Detection of hydrophilic or amphiphilic compounds with GC/MS is possible after derivatization or transformation of the target compounds to more volatile species (e.g. Giger 2009). However, several studies were focused on specific target compounds or compound groups and neglected other substances which were probably also present in the effluents (e.g. Rodriguez et al. 2004; Schriks et al. 2010). Other studies applied a screening approach in order to identify a preferably wide spectrum of organic contaminants (e.g. Ellis et al. 1982; Botalova et al. 2009). Although such approaches allow for the identification of numerous contaminants, there are still many substances which are detectable by GC/MS but remain unidentified because of their unknown mass spectra. The structure elucidation of such compounds is time consuming and includes interpretation of mass spectra and chemical synthesis of reference compounds. Other compounds might have physico-chemical properties which do not allow for the detection with GC/MS, which requires the application of more specific compound extraction, separation and detection methods. The organic compounds identified in different industrial effluents were listed in Table 2.1. It is indicated if only a certain compound group from the respective study was selected. Unspecific organic compounds which might also have a biogenic origin such as *n*-alkanes, fatty acids and fatty acid esters were not included.

In effluents from the *textile industry*, i.e. dye manufacturing plants and textile mills in the United States, several environmentally relevant compounds like halogenated anilines, benzenes and anthraquinones were found (Games and Hites 1977). Applying headspace techniques and GC/MS, also volatile organic solvents were determined in textile industry effluents (Smith 1990; López-Grimau et al. 2006). Screening analyses of untreated wastewaters revealed the presence of a wide spectrum of contaminants including different alkylated phenols and phthalic acid esters

Table 2.1 Organic compounds identified in industrial wastewaters applying different separation techniques and mass spectrometry

Industry	Identified organic compounds	Region	Wastewater type	Method	Type of listed compounds	Reference
Textile industry	Anisole, aniline, chloroaniline, alkylated anilines, dibromoaniline, tribromoaniline, hydroxyethylbutylbromoaniline, bromonitroaniline, bromodinitroaniline, hydroxyethylbutylaniline, bromodiethylaniline, hydroxyethylcyanoethylaniline, methylmethoxyaniline, nitrochlorobenzene, bromonitrobenzene, methoxyazobenzene, alkylated indolines, trimethylindole, trimethylloxindole, trimethylindolineacetaldehyde, dimethylindolinediacetaldehyde, chlorophenylthiadiazol, aminophenylthiadiazole, dichlorobenzene, hydroxyanthraquinone, dihydroxyanthraquinone, nitrobenzene, aminoanthraquinone, hydroxyaminoanthraquinone, bromoaminohydroxyanthraquinone, caprolactam, dinitrophenol, acetyllethylcyanoethylethoxyphenylenediamine	US	Effluents	GC/MS		Games and Hites (1977)
	Perchloroethylene, alkylated cyclohexanes, decahydronaphthalene, xylene, ethylbenzene, trimethylbenzene, methyl/ethylbenzene, trichlorobenzene, chloroisocyanatobenzene, dichloromethane, terpenes, chlorocyclohexanone, dibutylphthalate, chloroform, toluene	US	Effluents	Purge and trap prior to GC/MS		Smith (1990)
	Nitrobenzene sulfonate, methylbenzene sulfonate, chlorobenzene sulfonate, naphthalene sulfonates, alkylated benzene sulfonates	Spain, Portugal	Untreated	IPC-ESI-MS		Alonso et al. (1999)

(continued)

Table 2.1 (continued)

Industry	Identified organic compounds	Region	Wastewater type	Method	Type of listed compounds	Reference
	Ionol, di- <i>tert</i> .-butylethylphenol, di- <i>tert</i> .-butylmethoxymethylphenol, tetramethylbutylphenols, nonylphenols, methylenebisphenol, di- <i>tert</i> .-butylhydroxybenzoic acid, benzoic acid phenyl ester, dimethylphenylacetophenone, hexamine, <i>tert</i> .-butylquinone, diethylphthalate, dimethylcarboxymethylhexylphthalate, phenol, butylethylhexylphthalate, butyloctylphthalate, di-iso-octylphthalate, benzylbutylphthalate, benzylquinoline, tributylacetyl citrate, diethylaminomethylbenzopyranone, triphenylphosphonic acid	Portugal	Untreated	HT-GC/MS		Castillo and Barceló (2001)
	Polyethylene glycol, carboxylated polyethylene glycols, alkylalcohol polyethoxylate, dibutylphthalate, bis(ethylhexyl)phthalate, LAS, naphthalene sulfonates	Portugal		LC/MS		Castillo and Barceló (2001)
	Xylene, ethylbenzene, toluene	Spain	Effluents	SPME prior to GC/MS		López-Grimau et al. (2006)
	Bisphenol A, nonylphenol, octylphenol, nonylphenol ethoxylates, nonylphenol ethoxycarboxylates, octylphenol ethoxylates, octylphenol ethoxycarboxylates	Belgium, Italy	Effluents	LC/MS-MS		Loos et al. (2007)

Tanneries		Germany	Untreated	GC/MS screening	Reentisma and Jekel (1997)
Mercaptobenzothiazole, dihydroxypyrimidine, ethylhexylacetate, tris(butoxyethyl)phosphate, trimethylcyclohexanone, trimethylcyclohexenone, trimethylcyclohexanol, benzoic acid, cyclohexanecarboxylic acid, phenylacetic acid, phenylpropionic acid, methoxycinnamic acid, phthalic acid, phenol, cresol, chlorocresol, hexanol, ethylhexanol, hexandiol, glycerol, hydroxyindole, indole acetic acid, hydroxyphenylacetic acid, phenylacetic acid, hydroxyphenylacetic acid, dihydroxyphenylacetic acid, phenylacetic acid methyl ester, vanillylpropionic acid, dihydroxyphenylpropionic acid, methanoldiethoxylate, butanoldiethoxylate, pentanoldiethoxylate	Nitrobenzene sulfonate, chlorobenzene sulfonate, naphthalene sulfonates, alkylated benzene sulfonates	Portugal	Untreated	IPC-ESI-MS	Alonso et al. (1999) and Alonso and Barceló (1999)
Nitrobenzene sulfonate**, chlorobenzene sulfonate*, naphthalene sulfonates	Polyethylene glycol, alkylalcohol polyethoxylates, nonylphenol ethoxylates, carboxylated polyethylene glycols, bis(ethylhexyl)phthalate, diethylphthalate, nitrophenol, chlorocresol, nitrobenzene sulfonate, chlorobenzene sulfonate, LAS, naphthalene sulfonates, methylthiobenzothiazole, methylsulfinylbenzothiazole, benzothiazolylbenzothiazolethione	Sweden, Spain Portugal	Untreated	IPC-ESI-MS	Alonso and Barceló (1999)
LAS, polyethylene glycol, alkylalcohol polyethoxylates, naphthalene sulfonates, naphthalenedisulfonates, chlorobenzene sulfonate	Mercaptobenzothiazole	Sweden	Effluents	LC/MS	Castillo et al. (2001)
		Mexico	Effluents	HPLC-ED	Rodríguez et al. (2004)

(continued)

Table 2.1 (continued)

Industry	Identified organic compounds	Region	Wastewater type	Method	Type of listed compounds	Reference
Petrochemical Industry	Xylene, styrene, methylstyrene, indane, indene, methylindene, alkylated naphthalenes, phenol, cyclooctadiene, isopropylbenzene, ethyltoluene, butoxyethanol, acetophenone, terpineol, acenaphthene, fluorene, diphenylpropanol, cresol, acenaphthylene	US	Petrochemical & petrorefinery effluents	GC/MS		Keith (1974)
	Toluene, C ₂ -benzene, naphthalene, alkanones, phenol, ethylacetate, ethyl-iso-propylether, dioxolane, chlorobenzene, nitrobenzene, dimethyltoluenesulfonamide, azolidinylbutene, pyrrolidinylmethylethylbutane, prometone, simazine	US	Refinery effluents	GC/MS screening		Ellis et al. (1982)
	Benzene, toluene, ethylbenzene, xylenes, ethylmethylbenzene, trimethylbenzene, naphthalene	Ireland	Petrochemical effluents	SPME prior to GC/MS		James and Stack (1997)
	Ethylbenzoate, nonylphenol, pentachlorophenol, isothiocyanate-cyclohexane, tetramethylthiourea, bis(ethylhexyl)phthalate, methylpyrrolidinone, di-iso-octylphthalate, dimethylphthalate	Europe	Petrochemical effluents	LC/MS		Castillo et al. (1998)
	Dimethylbenzoic acid, trimethylbenzoic acid, ionol, di- <i>tert</i> -butylphenol, di- <i>tert</i> -butylethylphenol, ethylethoxybenzoate, diethylphthalate, butyloctylphthalate, di-iso-octylphthalate, dimethylphenylacetophenone, <i>tert</i> -butylhydroxymethylphenylsulfide	Portugal	Petrochemical effluents	HT-GC/MS		Castillo et al. (1999b)
	Chlorinated benzenes, chlorotoluene, chlorinated phenols, trichlorobenzaldehyde	Poland	Coking plant effluents	GC/MS		Czaplicka(2003)

Pulp and paper industry

Indoline, toluamide, alkylated+hydrogenated quinoline derivatives, N-phenylformamide, N- <i>tert</i> -butylbenzamide, tetramethylated piperidinone, triphenylphosphine oxide, alkylindanes, dimethylpyridine, PAHs and alkylated PAHs	Germany	Petrochemical effluents	GC/MS screening	Only source-specific constituents	Botalova et al. (2009) and Botalova and Schwarzbauer (2011)
Terpenes, methyltrisulfide, hexachloroethane, formylthiophene, acetylthiophene, propionylthiophene, dimethylsulfoxide, ethylcarbamate, nitrotoluene, dimethylsulfone, hydroxybenzaldehyde, hydroxyacetophenone, resin acids, trimethoxyacetophenone, trimethoxybenzaldehyde, methylthiobenzothiazole	US	Effluents	GC/MS screening		Keith (1976)
Dichlorocatechol, trichlorocatechol, monochlorotrihydroxybenzene, dichlorotrihydroxybenzene, trichlorotrihydroxybenzene, dichlorodihydroxymethoxybenzene	Norway	Chlorination stage effluents	GC/MS		Carlberg et al. (1980)
Chlorinated phenols, dichloroguaiacol, trichloroguaiacol, tetrachloroguaiacol	Switzerland	Effluents	GC/MS		Leuenberger et al. (1985)
Trichlorophenol, trichloroguaiacol, dehydroabiatic acid, chlorodehydroabiatic acid, dichlorodehydroabiatic acid	Sweden	Treated and untreated wastewater	GC/MS		Hynning (1996)
Nonylphenol ethoxycarboxylates	US	Effluents	GC/MS		Field and Reed (1996)
Nitrilotriacetic acid, EDTA, DTPA	Canada	Effluents	GC/MS		Lee et al. (1996)
Nitrophenol, chlorinated phenols, catechol	Europe	Effluents	LC/UV		Castillo et al. (1997)
Bisphenol A, mono-, di-, tri- and tetra-chlorinated bisphenol A	Japan	Effluents	GC/MS		Fukazawa et al. (2001)
Resin acids, bisphenol A, nonylphenol ethoxycarboxylates, lignin, polychlorinated dibenzothiophene, chlorinated phenols, chloroguaiacols, chlorosyringol, volatile sulphur compounds	Europe	Effluents	Various	Only compounds in effluents	Latorre et al. (2005) and references therein

(continued)

Table 2.1 (continued)

Industry	Identified organic compounds	Region	Wastewater type	Method	Type of listed compounds	Reference
	Ditolylmethane, ditolylethane, di-iso-propylnaphthalene, bis(methylphenoxy)ethane, terphenyl, benzyl-naphthyl ether, chloromethylphenoxy-methylphenoxyethane, benzylbiphenyl	Japan	Effluents	GC/MS		Terasaki et al. (2008)
	Terpenes, acetylmorpholine, aniline, trimethylpentane-di-ol-di-iso-butyrate, methanol, phenol, alkylated phenols, decalone, acetyloxytrimethylbicycloheptanedione, benzoic acid, abietic acid, dehydroabietic acid, hexahydrodimethyl-iso-propylnaphthalene	Germany	Effluents	GC/MS screening		Botalova and Schwarzbauer (2011)
Rubber and tire production	Benzothiazole, mercaptobenzothiazole, toluene, butoxyethanol, nonylphenol, di- <i>tert</i> -butyl-methylphenol, methylenediphenol, alkylated benzenes, isophorone, methylbiphenyl, cyclohexylamine, diphenylamine, propyldiphenylamine, diethylphthalate, naphthalene, alkylated naphthalenes, phenanthrene, alkylated phenanthrenes, fluoranthene, pyrene, dimethylacridan	US	Effluents	GC/MS		Jungclauss et al. (1976)
	Benzothiazole, methylbenzisothiazole, methylbenzothiazole, methylthiobenzothiazole, benzothiazolone, benzisothiazolol, thiocyanic acid (benzothiazoylthio) methyl ester, dithiobenzothiazol aniline, alkylated anilines, chlorinated anilines, benzoic acid, phenyl(phenylmethyl)thiourea, thiocyanic acid anilino-phenyl ester chlorobenzene, toluene, benzene isothiocyanate, methylamine benzoic acid, (methylthio) methylbenzene, (methylthio)benzoic acid, hydroxybenzoic acid, aminebenzoic acid, cyclohexylamine, benzoic acid hydroxymethylmethyl ester, diphenylhydrazinecarboxamide, methanetetraylbis-cyclohexanamine, methylimidazolidione, benzotriazinone	Spain	Partially treated wastewater	GC/MS		Puig et al. (1996)

Chemical production sites	Thailand	Effluents	GC/MS screening	Frequently occurring compounds	Worawit (2006)
Synthesis of e.g. pharmaceuticals, pesticides, optical brighteners and surfactants	Indole, methylindole, methyloxindole, diethylphthalate, dibutylphthalate, dicyclohexylphthalate, methoxyphenol, di- <i>tert</i> -butylphenol, mercaptothiazoline, zinc dimethylthiocarbamate, acetylphenylamine				
	Aminoethyldibenzoazepine, hydroxy- <i>tert</i> -amylphenylline, phenylphenylamine, dimethylquinoxaline, phenylphenylamine, tetramethylbutylphenylphenylamine, methylthiobenzothiazole, benzothiadiazole, nitrophenol, <i>tert</i> -amylphenol, di- <i>tert</i> -butylnitrophenol, di- <i>tert</i> -amylcyanophenol, di- <i>tert</i> -amylcyanomethylphenol, propylcarboxymethyl di- <i>tert</i> -butylhydroxyphenylpropionate, trifluoromethylaniline, di- <i>tert</i> -butylbenzoquinonemethideacetic acid, chlorinated diphenylether	US	GC/MS, LC/MS		Junglaus et al. (1978) and Lopez-Avila and Hites (1980)
Synthesis of 2,4,6-Trinitrotoluene	Nitrosomorpholine, nitrobenzonitrile, morpholinoacetonitrile, dinitrobenzene, trinitrobenzene, dimethyldinitrobenzene, methylnitrophenol, dinitromethylphenol, toluene, nitrotoluene, dinitrotoluene, trinitrotoluene, aminonitrotoluene, aminodinitrotoluene, dinitroaniline	US	GC/MS		Spanggord et al. (1982)
Synthesized compounds not indicated	Dimethoxymethane, dichloroethane, methylpentanol, styrene, methylbutadiene, propenenitrile, dichloromethane, toluene, methylpentanone, trivinylcyclohexane, divinylbenzene isomers	France	SPME prior to GC/MS		Santos et al. (1996)

(continued)

Table 2.1 (continued)

Industry	Identified organic compounds	Region	Wastewater type	Method	Type of listed compounds	Reference
Synthesis of e.g. plastics, lacquers and plant protection agents	LAS, naphthalene sulfonates, hydroxynaphthalenedisulfonate, nitrobenzene sulfonate, methylbenzene sulfonate, chlorobenzene sulfonate	Germany	Effluents	LC/MS		Castillo et al. (2001)
Synthesis of industrial intermediates and vitamins	Triphenylphosphineoxide, di-iso-propylidenesorbofuranose, di-iso-propylidenexylohexulofuranosic acid, bis-ethyl-iso-octanol lactone isomers	Germany	Effluents	GC/MS, LC/ESI-MS ^a		Knepper and Karrenbrock (2006)
Synthesis of e.g. plastics, flame-retardants and plant protection agents	Dichlorobenzene, chlorinated anilines, dichloromethylthiobenzene, trifluoromethylacetophenone, tetramethylbutane dinitrile, diphenylpropenenitrile, tetrahydrothiophene dicarboxylic acid, tris(chloropropyl) phosphates, triethylphosphate, dibutylmethylphosphonate	Germany	Effluents	GC/MS screening		Botalova et al. (2011)
Synthesis of various intermediate products	Dimethylpyrazol, tributylamine, tri-iso-octylamines, trioctylamine, tris(ethylhexyl)amine, dibutyldecamine, trithiolane, methyl diazadamanthane, tris(chloropropyl) phosphates, trimethylpentanediol-diisobutyrate, hydroxydimethylpropanoic acid hydroxydimethylpropylester	Germany	Effluents	GC/MS screening		Botalova et al. (2011)
Synthesis of e.g. fibers, lacquers and paints	Dimethylpyrazol, dithiolane, dithiane, trithiolane, trithianes, tetrathiane, tetrathiepane, hexathiepane, triacetin	Germany	Effluents	GC/MS screening		Botalova et al. (2011)
Pharmaceutical industry	Cimetidine, bromazepam, diclofenac, decahydroquinoline, metharbital	Germany	Effluents of a pilot treatment plant	FIA-MS-MS, GC/MS, LC/MS		Schröder (1999)

Food-processing industry Pea, fish and porc production Meat production Cement industry Automotive industry Power station	Hydroxyandrostanone, androstanedione	Germany	Effluents	GC/MS screening	Dsikowitzky (2002)
	Cortisol, cortisone, dexamethasone, prednisolone	Netherlands	Effluents	LC/MS	Schriks et al. (2010)
	Dichloropropane, toluene, trichloromethane, chlorinated phenols, diethylphthalate, bis(ethylhexyl)phthalate, fluorene, phenanthrene, fluoranthene, pyrene	Denmark	Effluents	Not specified	Maya-Altamira et al. (2008)
	Dibenzylamine, methylindolinone, tris(chloropropyl) phosphate, dihydrodimethylthiopyranecarboxaldehyde, <i>tert</i> .-butylbenzoic acid	Germany	Effluents	GC/MS screening	Botalova and Schwarzbauer (2011)
	LAS, naphthalene sulfonates	Germany	Effluents	LC/MS	Castillo et al. (2001)
	Hexamethoxymethylmelamine, butoxyethoxypropanol	Spain	Effluents	GC/MS	Consejo et al. (2005)
	Nitrosomorpholine, benzylidenebenzamine, benzybenzamide, tris(chloroethyl)phosphate, tris(chloropropyl) phosphate, trimethylphosphate, trimethylpentanedioildi-iso-butyrate, menthol, ethylhexanoic acid ethylhexyl ester, <i>tert</i> .-butylbenzoic acid, methylidihydro jasmonate, alkylated naphthalenes	Germany	Effluents	GC/MS screening	Botalova and Schwarzbauer (2011)

(Castillo and Barceló 2001). Phthalic acid esters are used in great quantities as plasticizers and the annual worldwide production volume was estimated to 5.2 million tons (Mackintosh et al. 2006). In untreated wastewaters, also different naphthalene sulfonates, benzene sulfonates and LAS were detected (Alonso et al. 1999; Castillo and Barceló 2001). Naphthalene sulfonates and anthraquinone sulfonates are employed as starting material for the manufacturing of azo and anthraquinone dyestuffs, and LAS are used as surfactants in detergent formulations (e.g. Fichtner et al. 1995). Whereas LAS are readily biodegradable, naphthalene sulfonates are relatively persistent and were also found in river water samples (Takada et al. 1994; Fichtner et al. 1995; Rieger et al. 2002). Untreated wastewaters and effluents from textile industries also contain compounds which are known as endocrine disrupting chemicals (Castillo and Barceló 2001; Loos et al. 2007). Nonylphenol, nonylphenol ethoxylate, octylphenol, diethylphthalate, bis(ethylhexyl)phthalate and bisphenol A are weakly estrogenic (Petrovic et al. 2004). Azo dyes are the largest group of dyes and account for more than half of the worldwide annual dye production (Stolz 2001). During the degradation of azo dyes, metabolites can be performed, which are themselves problematic for aquatic systems, e.g. 6-Acetylamino-3-aminonaphthalene-2-sulfonic acid, *N*-(bis-hydroxymethyl-phenyl)-acetamide, different aromatic amines and different anilines (Chung and Stevens 1993; Bhaskar et al. 2003; Pinheiro et al. 2004; Bilgi and Demir 2005) (see also Sect. 2.3).

Just like in untreated wastewaters of the textile industry, naphthalene sulfonates, benzene sulfonates and LAS were detectable in effluents and in untreated wastewaters from *tanneries* (Table 2.1) (Castillo et al. 1999a, 2001; Alonso et al. 1999; Alonso and Barceló 1999). Untreated wastewaters also contained the endocrine disrupting compounds nonylphenol ethoxylates, diethylphthalate and bis(ethylhexyl)phthalate (Castillo et al. 1999a; Petrovic et al. 2004). The leather industry uses nonylphenol ethoxylates and alkylalcohol polyethoxylates as surfactants to remove skin grease, whereas polyethylene glycol is used as leather lubricant. All these chemicals as well as carboxylated polyethylene glycols, which are very likely a degradation product of polyethylene glycol and alkylalcohol polyethoxylates, were present in the tannery wastewaters (Castillo et al. 1999a, 2001). Benzothiazoles are widely used as fungicides instead of chlorophenols and were also frequently found in tannery wastewaters (Reemtsma and Jekel 1997; Castillo et al. 1999a; Rodriguez et al. 2004). A comprehensive investigation revealed that untreated tannery wastewaters were heavily burdened with organic compounds (DOC 900 mg l⁻¹) (Reemtsma and Jekel 1997). Numerous contaminants from 12 compound classes including cyclohexanes, aromatic carboxylic acids, phenols, indoles and ethoxylates were identified. After anaerobic and biological wastewater treatment, DOC concentration was strongly reduced and the contaminant concentrations of all compound classes decreased. Nevertheless, environmentally relevant compounds were still detectable after the treatment process (Reemtsma and Jekel 1994, 1997). Some of these contaminants were relatively persistent against the treatment process (e.g. benzothiazoles), others were newly performed during treatment like dichlorobenzoic acid and tris (2-butoxyethyl)phosphate (Reemtsma and Jekel 1997).

Several studies focused on the chemical characterization of effluents from the **petrochemical industry**, i.e. petroleum refining and related industries. Important petroleum products are gaseous fuels, gasoline, solvents, lubricating oil, grease, waxes and asphalt. During the distillation of crude oil in the refineries, fractions with different physico-chemical properties are obtained. Alkylated benzenes, indane and its alkylated derivatives as well as naphthalene were found in several effluent samples (Table 2.1) (Keith 1974; Ellis et al. 1982; James and Stack 1997; Botalova et al. 2009; Botalova and Schwarzbauer 2011). These compounds are e.g. constituents of the gas and naphtha fraction (Speight 2007). Alkylated naphthalenes and quinoline derivatives also occurred in effluent samples (Keith 1974; Botalova et al. 2009) and are characteristic constituents of the middle distillate fraction (Speight 2007). Further constituents of crude oil which were also present in effluent samples were indoline, acenaphthene, acenaphthylene and fluorene (Keith 1974; Ellis et al. 1982; Wang et al. 1998; Speight 2007). However, Botalova et al. (2009) reason that indoline and quinoline related compounds may also represent technical byproducts of secondary synthetic processes in petrochemical plants. The presence of xylene, toluene and benzene in effluents was reported in the three earliest studies (Keith 1974; Ellis et al. 1982; James and Stack 1997). These chemicals are primary products of oil refineries and are widely used as educts for a large variety of chemical synthesis, e.g. for the plastic production. By alkylation of toluene with ethylene, followed by hydrogenation, methylstyrene is obtained, which is used for polymerization synthesis (Speight 2007). Styrene and methylstyrene were found in effluent samples, as well as phenol and nitrobenzene (Keith 1974; Ellis et al. 1982). The latter two compounds are e.g. used for the solvent refining of lubricating oils in order to remove undesirable constituents from the charge material (Speight 2007). Phthalic anhydride is a precursor in the synthesis of phthalic acid esters which are used as plasticizers. It is produced in petrochemical plants by oxidation of naphthalene (Speight 2007). The occurrence of different phthalic acid ester derivatives in petrochemical effluents (Castillo et al. 1998, 1999b) could therefore result from the synthesis of starting materials for plastic production in these plants. This is underlined by the fact that ionol and ionol derivatives were also present (Castillo et al. 1999b), which are used as additives in plastic materials and rubber (Yasuhara et al. 1997). Further structurally very diverse compounds were detected in the effluent samples. Summing up, the chemical composition of the petrochemical plant and refinery effluents was found to be very heterogenic. From this it follows that the production processes in the plants and refineries and the wastewater treatment approaches differ strongly which leads to a unique chemical composition of the effluents.

Studies on the chemical characterization and toxicity of wastewaters from the **pulp and paper industry** were recently reviewed (Latorre et al. 2005). Contaminants which were identified in pulp and paper production effluents as indicated in this review and information from further studies are presented in Table 2.1. Generally, the effluents contain natural plant constituents such as resin acids (e.g. abietic and dehydroabietic acid), lignin, terpenes, catechol, hydroxybenzaldehyde, and structurally related compounds. The bleaching of chemical pulp with chlorine leads to

the presence of the chlorinated derivatives of plant constituents: chlorinated catechols, chlorinated dehydroabietic acid, chlorinated guaiacols and chlorinated syringols. Chlorinated phenols were formerly used as wood preservatives and as a result they have also been encountered in effluent samples (Latorre et al. 2005). Paper mill effluents also contained bisphenol A and nonylphenol ethoxycarboxylates (Field and Reed 1996; Latorre et al. 2005), which were shown to be weakly estrogenic (White et al. 1994; Petrovic et al. 2004). Bisphenol A is a common raw material in the paper production (Fukazawa et al. 2001). The compound is easily chlorinated by the bleaching and disinfection agent sodium hypochlorite, and chlorinated bisphenol A derivatives are performed, which were identified in effluent samples (Fukazawa et al. 2001). During the last decade, the use of chlorine as bleaching agent was reduced and it was replaced by chlorine dioxide, molecular oxygen, peroxide or ozone (e.g. Latorre et al. 2005). The elimination of chlorine as bleaching agent caused the launching of metal binders such as DTPA and EDTA in the paper recycling industry, and their occurrence in the respective effluents. These agents bind metals which would otherwise disturb the bleaching process with hydrogen peroxide (Lee et al. 1996). The replacement of chlorine by other bleaching agents also explains the absence of chlorinated compounds in the two most recent studies from Japan and Germany. The compounds detected in sediment samples from the outfall of the largest paper mill industry area in Japan are used as solvents and color sensitizers in the manufacture of thermal paper (Terasaki et al. 2008). Besides terpenes and resin acids, a photoinitiator (acetyloxytrimethylbicycloheptanedione) and an adsorbent (acetylmorpholine) were found in German effluents from a paper production facility (Botalova and Schwarzbauer 2011). The other effluent constituents were unspecific.

In effluents from **rubber and tire production** plants, structurally diverse organic compounds were detected, of which many are known as chemicals frequently used in the rubber industry (Table 2.1). The presence of benzothiazoles and aniline derivatives in effluents was proved in two studies (Jungclaus et al. 1976; Puig et al. 1996) and arises from the use of benzothiazoles and aniline derivatives as catalysts for the vulcanization process (Fishbein 1991). Different phthalic ester derivatives, i.a. diethylphthalate, dibutylphthalate and dicyclohexylphthalate were also detected (Jungclaus et al. 1976; Worawit 2006), being related to the use of phthalic esters as plasticizers in the rubber production (Fishbein 1991). Toluene is used as solvent for rubber processing, di-*tert*.-butylmethylphenol and structurally related compounds are employed as antioxidants. Other important antioxidants are diphenylamines (Fishbein 1991), which can explain the presence of diphenylamine and propyldiphenylamine in the effluent samples from the US. Mineral oils and tar products are widely used in the rubber industry as extenders (Fishbein 1991 and references therein). They contain PAHs, such as naphthalene and phenanthrene and their alkylated derivatives as well as fluoranthene and pyrene, which were all found in the effluents (Jungclaus et al. 1976). Further compounds were detected in the effluents, some of them are structurally related to the compounds described above, but their specific application in the rubber and tire production is unknown.

Due to the wide spectrum of industrial chemicals which are synthesized at **chemical production sites**, the chemical composition of effluent samples is very heterogeneous. For example, different nitrogen containing heterocyclic compounds, sulfur containing compounds and chlorinated compounds were identified in an early study of effluents from a chemical production site in the US (Jungclaus et al. 1978; Lopez-Avila and Hites 1980). During the synthesis of the explosive trinitrotoluene, wastewaters are generated, which are heavily polluted with nitroaromatic compounds, including nitrotoluenes, nitrobenzenes, nitroanilines and nitrobenzonitrile (Spanggord et al. 1982). Effluents from industries which produce modern plastic materials, industrial intermediates, plant production agents and flame retardants contained a completely different spectrum of contaminants (Table 2.1) (Botalova et al. 2011). Many of them are unspecific and also occur in municipal effluents. These are, for example, surfactants such as LAS, flame retardants such as alkyl phosphates and the plasticizer trimethylpentanedioldi-iso-butyrate (e.g. Eganhouse 1986; Dsikowitzky 2002). Other compounds were described to stem exclusively from industrial emission sources, e.g. hexathiepane. Tetramethylbutanedinitrile, several identified tertiary amines and triacetin are potential site-specific markers for the characteristic production processes taking place in three chemical manufacturers, respectively (Botalova et al. 2011). Another study exclusively described byproducts which are performed during specific chemical synthesis. Such compounds are manufactured unintentionally and have no commercial application. Accordingly, little attempts have so far been made to gather information about their properties, their toxicities and their fate in the environment (Knepper and Karrenbrock 2006). Similar to textile industry and tannery wastewaters, naphthalene sulfonates, benzene sulfonates and LAS were detectable in effluents from a manufacturer of plastic materials, lacquers and plant protection agents (Castillo et al. 2001). The analysis of effluents from a chemical manufacturer in France (Santos et al. 1996) revealed the presence of different solvents, which are widely known as water pollutants.

As in the chemical manufacturing, the production processes in the **pharmaceutical industry** are very diverse and depending on the manufactured medicines, which is mirrored by complete different chemical compositions of the effluents (Table 2.1). Effluents of a German pilot treatment plant contained the antihistamine cimetidine, the tranquilizer bromazepam, the pain reliever diclofenac and the anticonvulsant metharbital (Schröder 1999). Mainly steroids which are structurally related to androsterone were found in effluents from another German company. They are probably byproducts of the manufacturing of hormone supplements (Dsikowitzky 2002). Further steroid hormones including cortisol, cortisone, dexamethasone and prednisolone were determined in pharmaceutical industry effluents in the Netherlands (Schriks et al. 2010).

We found a rather limited number of studies about effluents from other industrial facilities such as the food-processing industry, cement industry, automotive industry and a power station (Table 2.1). Information about the emissions of the coating and printing industry and of manufacturers of electric devices, toys and computers would be interesting, but are lacking.

Several compound groups appeared in many different industrial effluent types including benzene and naphthalene sulfonates, phthalic acid esters, volatile organic

solvents, chlorinated benzenes, phenol and alkylphenols. It illustrates that they are unspecific and implies that their occurrence in the environment does not allow for attributing their presence to certain emission sources. The analytical approaches determine the set of compounds which are detectable in the samples. Compound groups which were addressed frequently were sulfonates and endocrine disrupters. However, screening studies illustrated that emerging environmental contaminants might be generated during wastewater treatment and released to aquatic systems, which are not addressed by monitoring studies. This applies also to byproducts of industrial synthesis. The replacement of environmentally problematic compounds by novel industrial formulation is common and leads to the occurrence of further emerging contaminants in the effluents with unknown impact in the environment.

Overall, the heterogeneity of the chemical composition of effluents from similar industries is striking. The observed differences are related to different industrial production processes, leading to the presence of varying synthesis educts, additives, products and byproducts in the wastewaters. For wastewater treatment, different techniques are applied which exhibit different efficiencies in contaminant removal. Chemical materials are synthesized in batches, leading also to short-term fluctuations in the effluent composition. Many authors addressed these fluctuations and generated composite samples or carried out multiple sampling sessions.

Given the diversity of the production processes and high structural diversity of the effluent constituents, further studies on effluents from chemical production sites, petrochemical and pharmaceutical industry should be carried out. These industries emit a plentitude of structurally diverse organic contaminants. Many of these compounds might be stable in aquatic systems, but their occurrence has not been reported yet and no information is available about their distribution in the environment and their ecotoxicological relevance.

The occurrence of the described compounds in industrial effluents does not indicate their persistence in the environment. The fate of industrial contaminants in aquatic systems is discussed in Sect. 2.3.

2.3 Tracing Industrial Wastewaters in the Environment

In this section, studies on the occurrence and fate of industrial contaminants in aquatic systems are discussed. Only studies are selected, which applied a comprehensive chemical characterization of the samples, and in which the identified contaminants were unequivocally attributed to industrial emissions. Although various studies were published which focus on the occurrence of organic contaminants in industrial wastewaters (Sect. 2.2.2), relatively few studies were found which survey the fate of industrial contaminants in aquatic systems (Table 2.2).

Two early studies were groundbreaking for this topic. Organic contaminants were identified in effluents of a chemical production site (Table 2.1) and subsequently traced in the adjacent river water course and coastal waters (Table 2.2) (Jungclauss et al. 1978 and Lopez-Avila and Hites 1980). The chemical composition

Table 2.2 Organic compounds which were detected in water, sediment or animal samples and could unequivocally be attributed to industrial emissions

Industry	Detected organic compounds	Region	Concentration range	Compartment	Reference
Textile industry	Aminoalcoholphenoxanthracenedione (CI disperse Red 60), dihydroxybis(methylamino)anthraquinone (CI disperse blue 26), acetamidooxyethoxybromodinitrophenyldiazonylme-thoxyanilinoethyl acetate (CI disperse blue 79), bromodinitroaniline	Canada	nq	River water, sediment	Maguire (1992)
	Acetylaminobis(methoxyethyl)aminomethoxyphenylaminobromochlorobenzotriazole, acetylaminocyclohexylaminomethoxyphenylaminobromochlorobenzotriazole, acetylaminohydroxyethylaminomethoxyphenylaminobromochlorobenzotriazole	Japan	nq	River water	Nukaya et al. (1997), Oguri et al. (1998), and Shiozawa et al. (2000)
	Aminodichlorobenzotriazole	Korea	nq	River water	Kwon et al. (2003)
	Bromodinitrophenyldiazonyldipropenylaminomethoxyphenylacetamide (CI disperse Blue 373)	Brazil	nq	River water	Umbuzeiro et al. (2005)
Tanneries	Ethylacetate, ethanol, methylpentanone, toluene, methylpropanol, butanol, ethoxyethanol, butoxyethanol, bis(dimethylaminoethyl)ether, hexanediol, ethylhexanol, dimethylbenzylalcohol, butoxyethoxyethanol, hexylglycolmono-iso-butyrate, di-tert.-butylmethylphenol, phenol, cresol, di-tert.-butyldimethylbicyclohexanone	Japan	9–5,680 µg l ⁻¹	River Water	Yasuhara et al. (1981)
	Tribromomethane	Greece	98,000 ng/l	Coastal water, water from canals and marshes	Grigoriadou et al. (2008)
Petrochemical industry	Dimethylpyridine, thioanisole	Germany	<5–130 ng l ⁻¹	River water	Botalova and Schwarzbauer 2011
	Alkylated naphthalenes, alkylated phenanthrenes/anthracenes, alkylated dibenzothiophenes, alkylated biphenyls	Indonesia	0.005–20 µg g ⁻¹ dw	Coastal sediment	Dsikowitzky et al. (2011)

(continued)

Table 2.2 (continued)

Industry	Detected organic compounds	Region	Concentration range	Compartment	Reference
	Alkylated naphthalenes, alkylated phenanthrenes/anthracenes, alkylated dibenzothiophenes, alkylated biphenyls, triphenylphosphine oxide, triphenylphosphine sulfide	Indonesia	nq	Mangrove macrobenthic invertebrates and fish	Diskowitzky et al. (2011)
Pulp and paper industry	Chlorophenols, chloroguaiacols, chlorocatechols, resin acids	Finland	200–20,400 ng l ⁻¹	Lake water	Oikari et al. (1985)
	Chlorophenols, chloroguaiacols, chlorosyringols, chlorocatechols	Sweden	12–3,710 ng l ⁻¹	Coastal water	Söderström et al. (1994)
	Chlorophenols, chloroguaiacols, chlorosyringols, chlorocatechols	Sweden	0.027–48.7 µg g ⁻¹	Marine fish bile	Söderström et al. (1994)
	Chlorophenols, chloroguaiacols, chlorocatechols	Finland	Not indicated	Coastal sediment	Palm and Lammi (1995)
	Chlorophenols, chloroguaiacols, chlorovanillins, chlorocatechols, chlorinated dehydroabietic acids	New Zealand	<0.01–5.2 µg g ⁻¹ dw	Lake sediment	Tavendale et al. (1995)
	Nonylphenol ethoxycarboxylates	US	1,700–11,800 ng l ⁻¹	River water	Field and Reed (1996)
	Chlorophenols, chloroguaiacols, chlorovanillin, chlorocatechols	New Zealand	<0.01–0.0247 µg g ⁻¹ dw	River sediment	Judd et al. (1996)
	Chlorophenols, chloroguaiacols, chlorovanillin, chlorocatechols	Finland	2.1 µg ml ⁻¹	Fish bile	Leppänen et al. (1998)
	Resin Acids, sitosterol, wood sterols, chlorophenols	Finland	<0.1–3,290 µg g ⁻¹ dw	Coastal sediment	Meriläinen and Oikari (2008)
	Resin Acids, sitosterol, chlorophenols	Finland	<0.05–7,800 µg g ⁻¹ dw	Macrobenthic invertebrate and insect tissues	Meriläinen and Oikari (2008)

Rubber and tire production Chemical production sites Synthesis of e.g. pharmaceuticals, pesticides, optical brighteners and surfactants	Dimethyldiphenylmethane, dimethylphenylethane, di-iso-propylnaphthalene, bis(methylphenoxy)ethane, terphenyl, benzyl-naphthylether, diphenoxybenzene, benzylbiphenyl, dichloromethylphenoxyethane, dibenzylloxybenzene	Japan	130–5,290 ng l ⁻¹	Coastal water	Terasaki et al. (2012)
	Dimethyldiphenylmethane, dimethylphenylethane, di-iso-propylnaphthalene, bis(methylphenoxy)ethane, terphenyl, benzyl-naphthylether, chloromethylphenoxymethylphenoxyethane	Japan	1.6–190 µg g ⁻¹ dw	Coastal sediment	Terasaki et al. (2012)
	Dimethyldiphenylmethane, dimethylphenylethane, di-iso-propylnaphthalene, bis(methylphenoxy)ethane, terphenyl, benzyl-naphthylether, diphenoxybenzene, chloromethylphenoxymethylphenoxyethane, benzylbiphenyl, dichloromethylphenoxyethane, dibenzylloxybenzene	Japan	<0.01–0.0872 µg g ⁻¹ ww	Marine fish tissue	Terasaki et al. (2012)
	Benzothiazole, methylthiobenzothiazole, methylbenz-iso-thiazole, methylbenzothiazole, cyclohexylamine, toluene, aniline	Spain	nq	Irrigation canal water	Puig et al. (1996)
	Hydroxy- <i>tert</i> .-amylphenylbenzotriazole, hydroxy- <i>tert</i> .-butylmethylphenylchlorobenzotriazole, chloroethylamino-iso-propylaminotriazine, chlorobis(ethylamino)triazine, phenylnaphthylamine, tetramethylbutylphenyl-naphthylamine, toluidinesulfonylphenol, diphenylloctylphosphate, <i>tert</i> .-amylphenol, methoxydi- <i>tert</i> .-butylphenol, di- <i>tert</i> .-butylcyanophenol, di- <i>tert</i> .-amylcyanophenol, di- <i>tert</i> .-amylcyanomethylphenol, chlorophenylisocyanate, chlorotrifluoromethylphenylisocyanate, chlorophenyl-iso-propylcarbamate, chlorotrifluoromethylphenyl-iso-propylcarbamate	US	0.1–1,600 µg g ⁻¹	River and estuarine sediments	Jungclaus et al. (1978); Lopez-Avila and Hites (1980)

(continued)

Table 2.2 (continued)

Synthesis of industrial intermediates and vitamins	Di-iso-propylidenesorbofuranose, bis-ethyl-iso-octanol lactone isomers, di-iso-propylidenexylohexulofuranosic acid, triphenylphosphin oxide,	Germany	110–4,000 ng l ⁻¹	River water	Knepper and Karrenbrock (2006); Knepper et al. (2000)
Synthesis of e.g. plastics, flame-retardants and plant protection agents	Dichloroaniline, triethylphosphate, tributylphosphate, trimethylpentanediolediisobutyrate	Germany	<5–160 ng l ⁻¹	River water	Botalova and Schwarzbauer (2011)
Synthesis of industrial chemicals, e.g. polymers and solvents	Chloromethyldioxolane, triethylphosphate, trimethylbenzoic acid, <i>tert</i> -butylbenzoic acid	Germany	<5–530 ng l ⁻¹	River water	Botalova and Schwarzbauer (2011)
Synthesis of organochlorine pesticides	DDT, DDD, DDE, DDMU, DDA, DBP, DDCN, DDABE, DDAMA, CPE, MCPE, DCPE, HCHs, tetrachlorocyclohexene, pentachlorocyclohexenes, heptachlorocyclohexene, chlorinated benzenes, chlorinated benzoic acids, chlorinated phenols	Germany	<100–75,000,000 ng l ⁻¹	Groundwater	Frische et al. (2011)
Pharmaceutical industry	Chlorthalidone, torsemide, zolpidem, azithromycin, warfarin, desmethylazithromycin, erythromycin, dehydrated erythromycin, terbinafine	Croatia	0.8–20.1 µg g ⁻¹ dw	River sediment	Terzić and Ahel (2011)
Food- processing industry					
Meat production	Dibenzylamine, methylindolinone	Germany	6–18 ng l ⁻¹	River water	Botalova and Schwarzbauer (2011)

nq: not quantified dw: dry weight ww: wet weight

The contaminant concentrations in animal tissue and sediments were listed as dry weight or wet weight values, if this information was indicated in the references

of the river water reflected the effluent discharge and the aqueous concentrations of the various compounds followed the rule of simple dilution. The compounds with the highest octanol-water coefficients were found to be strongly associated with particulate matter and were detectable in the sediments, also at the greatest distance from the plant, some of them in high concentrations. Namely benzotriazole, chlorobenzotriazole, diphenylether, trichlorodiphenylether, dibenzoazepine, triazine, phenylbutazone and phenylnaphthylamine occurred throughout the whole environmental system or were present at relatively high concentrations. Some of the compounds evaporated or degraded; for example, the degradation process involved the oxidation of dissolved phenols to quinones. It was concluded that the long-term exposure to this wide variety of contaminants contributed to the lack of biota in the receiving river water course.

Most of the later studies observed solely the fate of industrial contaminants in aquatic systems without the simultaneous characterization of contaminants in the effluents. Many of them were carried out in industrial nations of the northern hemisphere.

Aminodichlorobenzothiazole was identified for the first time in river water near a complex of the *textile industry* in Korea (Table 2.2) (Kwon et al. 2003). It is an educt for the synthesis of magenta dyes (EP Patent 0,468,380). Although the Ames test revealed no mutagenic activity of the compound, its presence in public waterways might need further attention due to the unknown effects on the health of humans and aquatic animals. Different dye stuffs and degradation products were also detected in other river systems (Maguire 1992; Nukaya et al. 1997; Oguri et al. 1998; Shiozawa et al. 2000; Umbuzeiro et al. 2005). Another study on riverine contamination by a leather *tannery* demonstrated the presence of relatively unspecific non-halogenated organic solvents in water samples (Yasuhara et al. 1981).

High concentrations of tribromomethane, dimethylpyridine and thioanisole were detected in water samples from the vicinity of *petrochemical industries* (Grigoriadou et al. 2008; Botalova and Schwarzbauer 2011). However, the origin of tribromomethane and thioanisole could not directly be linked to production processes in the petrochemical plants (Grigoriadou et al. 2008; Botalova and Schwarzbauer 2011). Different alkylated PAHs were detected in water, sediments, mangrove macrobenthos and fish from a tropical lagoon which receives wastewaters from a large oil refinery (Dsikowitzky et al. 2011). Alkylated PAHs are more abundant in crude oil and more persistent in the environment than parent PAHs (Barron and Holder 2003). This suggests their use for the tracing of petrogenic contamination rather than considering only a limited number of parent PAHs. Furthermore, triphenylphosphine oxide, a byproduct of the industrial production of olefins, was detected in many of the animal tissue samples from the tropical lagoon (Dsikowitzky et al. 2011). Its presence in petrochemical effluents was demonstrated (Botalova et al. 2009), but it also occurs in municipal sewage (Rodil et al. 2005).

The bleaching of chemical pulp with chlorine, which is a process frequently applied by the *pulp and paper industry*, results in the performance of chlorinated derivatives of plant constituents such as chlorophenols, chloroguaiacols, chlorovanillins, chlorosyringols and chlorocatechols (Sect. 2.2.2). Their presence in aquatic

systems was demonstrated in a number of studies, and they were detected in water, sediment and animal tissue (Table 2.2). A completely different compound spectrum was found in the vicinity of thermal paper manufacturing plants due to the different production processes. The chemical composition of the water, sediment and animal tissue from the plant vicinity reflected adequately the composition of the wastewaters (Tables 2.1 and 2.2) (Terasaki et al. 2012). Discharges of a **rubber and tire production facility** resulted in the presence of different derivatives of benzothiazole in a water irrigation channel (Tables 2.1 and 2.2) (Puig et al. 1996). The compounds remained intact after the purification process in the plant and were traced in the public waterways over more than 100 km distance from the source, indicating their stability.

Tetrabromobisphenol A, a brominated flame retardant, and its dimethylated derivative were found in high concentrations in sediment samples downstream a **chemical production site** in Sweden (Sellström and Jansson 1995). It was demonstrated that this particular production site emitted the tetrabromobisphenol A by analyzing circuit boards which are produced by the company and by analyzing sludge from a sewage treatment plant receiving leach water from a landfill with wastes from this plant. The circuit boards and the sludge samples contained high levels of the target compound. In sewage sludge samples from a treatment plant to which no known users of tetrabromobisphenol A were connected, and in sediment samples from upstream the plant, significantly lower levels of the compound were found.

Hexamethoxymethylmelamine was found in surface waters of the Netherlands (Bobeldijk et al. 2002). This compound is used as cross-linking agent in organic coatings and plastics. In Europe, industrial applications include coatings for cans, coils and automobiles (Weiss 1997). HMMM is also used for the formation of melamin nanoparticles and for the production of castings (e.g. Weber et al. 2009). The presence of this compound in surface waters is therefore likely related to its application in specific industrial production processes.

The presence of different chlorinated organic contaminants in Spanish river water reflected the impact of a chlorinated organic solvent factory in the vicinity of the sampling sites (Table 2.2). However, the tap water of the nearby village was not affected and the concentrations of chlorinated compounds were below safety thresholds for drinking water (Amaral et al. 1996). The city of Sumgayit in Azerbaijan was a center for the production of chlorinated industrial and agricultural chemicals of the former Soviet Union. In sediments from wetlands in the vicinity of the industrial complex, high concentrations of toxic organochlorine pesticides were found. In comparison to turtles from reference sites, significantly enhanced levels of all emitted pesticides were measured in two turtle species (*Mauremys caspica*, *Emys orbicularis*) from the wetlands (Swartz et al. 2003). Bitterfeld was an important industrial production complex for chlorinated organic compounds in the former German Democratic Republic. The industrial discharges were released to a brook which flows into the Mulde River, a tributary of the Elbe River. To date chlorinated naphthalenes have been reported in high concentrations in the brook sediments (Table 2.2) (Brack et al. 2003), as well as in Elbe River and Mulde River sediments

(Schwarzbauer, unpublished results). Organochlorine pesticides and other chlorinated organic compounds were also detected in groundwater samples from the vicinity of another production unit of the German Democratic Republic which was closed at the end of the 1980s (Frische et al. 2011). The presence of specific chlorinated contaminants downstream a modern chemical production site in Germany was attributed to the technical synthesis of low volatile chlorinated organic compounds in the plant (Dsikowitzky et al. 2004; Kronimus et al. 2004).

In another study, several types of organic contaminants were identified in industrial wastewaters of the chemical industry which were byproducts of specific production processes (Table 2.1). All of them were also traced in the Rhine River, Germany (Knepper and Karrenbrock 2006; Knepper et al. 2000) (Table 2.2). In river water samples taken downstream at different distances from several industrial point sources in Germany, a set of organic contaminants was identified, which were attributed to the specific discharges. Chloromethyldioxolane only occurred in samples taken downstream a chemical production site and was suggested as site-specific molecular marker (Botalova and Schwarzbauer 2011).

The presence of several pharmaceutical drugs in river sediments was unequivocally attributed to discharges of the *pharmaceutical industry*. Less known pharmaceutical intermediates and/or transformation products were identified, which had not been reported from freshwater sediments as yet (Terzic and Ahel 2011).

Only in comprehensive studies including industrial wastewaters *and* field samples, the compound spectra found in the wastewater samples could be retrieved in samples from the adjacent aquatic system. In all other cases, except the pulp and paper industry, the compound spectra found in field samples from industrialized areas (Table 2.2) was totally different from those in studies on effluents of the respective industries (Table 2.1). This illustrates again the complexity of the chemical composition of industrial wastewaters, even from the same industry types, and the lack of data about the related environmental impacts (see also Sect. 2.2.2). Screening analyses of the individual contamination profile of industrialized areas are therefore urgently required including the examination of wastewater samples *and* field samples.

Many well-known pollutants such as PCBs, chlorinated benzenes and flame retardants may either origin from industrial or from municipal sources (e.g. Blanchard et al. 2004; Law et al. 2006; Marti et al. 2011). Although their presence in industrialized areas suggests their industrial origin, they exhibit a lot of different applications and therefore cannot unequivocally be attributed to industrial emissions. Studies with a high spatial resolution covering upstream and downstream sampling at potential emission sites are necessary to demonstrate industrial inputs of such unspecific contaminants. It is therefore beneficial to identify industrial organic markers which allow the tracing of specific industrial emissions in the environment. The marker concept has been developed by geochemists to understand the sources, transport and fate of organic compounds. An ideal marker should be source specific and exhibit a conservative behavior. The source specificity refers to the link between a molecular marker and its source. The conservative behavior implies that the marker is stable over time scales relevant to the processes under study (Eganhouse

1997; Takada and Eganhouse 1998). Potential industrial organic markers should be characteristic for wastewaters from different industrial branches and for the specific industrial production processes which are applied.

These markers can then be used to verify the input of specific industrial wastewaters to aquatic systems and to investigate the spatial distribution of the emission. This information is vital to disentangle different emission sources and to further investigate their potential impacts in the environment. The generated knowledge can provide a scientific basis for the development of management measures for a reduction of the contamination. In Table 2.3, potential industrial organic markers for different emission sources are presented as synthesis of Sects. 2.2.2 and 2.3.

The listed compounds are source specific, meaning that their occurrence is related to specific industrial production processes. Due to their structural characteristics it can be excluded that they also occur in nature. Furthermore, they were detectable in field samples indicating their environmental stability. Therefore, they fulfill the criteria for marker compounds. The chemical structures of these potential industrial markers are presented in Fig. 2.2. Some of the compounds which were detected in the environment and were unequivocally attributed to a specific industrial source are known to occur also in municipal sewage such as triphenylphosphine oxide. These compounds were excluded. Future studies should verify the usefulness of the suggested industrial markers and identify more markers for specific industrial production processes.

2.4 Identification of Toxic Organic Contaminants in Industrial Wastewaters

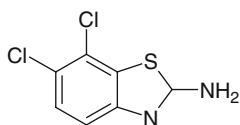
Toxicity tests with microorganisms and algae were successfully conducted to survey the toxic effects of industrial wastewaters before and after wastewater treatment (e.g. Chen et al. 1999; Kungolos 2005a, b). The approach allows to assess the reduction of the toxicity which is achieved by wastewater treatment and to estimate the impact of the treated wastewater on aquatic organisms. The toxicity of numerous single organic contaminants which are commonly found in industrial wastewaters was tested under laboratory conditions for different experimental species (e.g. Nestmann et al. 1980; Drzyzga et al. 1995; Ali and Sreekrishnan 2001).

The mentioned studies give evidence about the toxicity of specific industrial organic contaminants and different industrial wastewaters and are useful to estimate potential impacts in the environment. However, the causative constituents which are responsible for the observed toxicity of whole wastewater samples are not identified. To close this gap of knowledge, mainly two approaches are applied which combine chemical analysis and toxicity evaluation: (1) chemical characterization of wastewaters and toxicity evaluation, and (2) toxicity-based fractionation of the wastewater samples and thereafter identification of the compounds which caused the observed toxic effects. Both approaches are discussed in the following sections.

Table 2.3 Potential marker compounds which could be useful to trace industrial emissions in aquatic systems

Industry	Organic marker	Compartment	Production process
Textile industry	Aminodichlorobenzothiazole	Water	Educt in the synthesis of magenta dyes
	Azo dye stuffs such as CI Disperse Blue 373 and their metabolites	Water	Coloring of textiles
Petrochemical industry	Dimethylpyridine	Water	Refining of crude oil (compound is a constituent of tar)
	Alkylated dibenzothiophenes	Water, sediment, biota	Refining of crude oil (compounds are characteristic constituents of crude oil and therefore characteristic for petrogenic contamination)
	Chloroguaiacols, chlorovanillins, chlorocatechols, chlorinated dehydroabietic acids, chlorosyringols	Water, sediment, biota	Bleaching of chemical pulp with chlorine
Pulp and paper industry	Chloromethylphenoxymethylphenoxylethane, Bis(methylphenoxy)ethane, benzylbiphenyl ether, benzylbiphenyl	Water, sediment and/or biota	Application of sensitizers and sensitizer related compounds for the preparation of thermal paper
	Presence of numerous derivatives of benzothiazole	Water	Vulcanization
Rubber and tire production	Bis-ethyl-iso-octanol lactone isomers	Water	Butanal synthesis
	Di-iso-propylidenesorbofuranose, di-iso-propylidenexylhexulofuranosic acid	Water	Byproduct of the vitamin C synthesis
	Hexamethoxymethylmelamine	Water	Coating of metals
	Bis(chloropropyl)ethers, hexachlorobutadiene, octachlorostyrene	Sediment	Synthesis of chlorinated industrial chemicals
	Chloromethyldioxolane, hexachlorobutadiene, octachlorostyrene	Water	Synthesis of chlorinated industrial chemicals

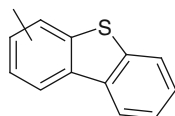
These compounds do not occur in municipal sewage, their origin can be attributed to specific industrial production processes and they were detectable in industrial areas. They can be used to verify the input of specific industrial wastewaters to aquatic systems and to investigate the spatial distribution of the emission



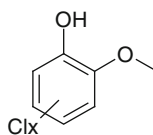
2-Amino-6,7-dichlorobenzothiazole
CAS No. 24072-75-1



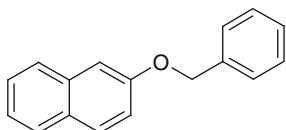
Dimethylpyridine



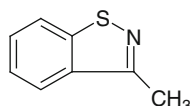
Methyldibenzothiophene



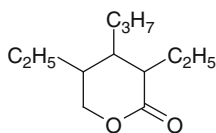
Chloroguaiacols



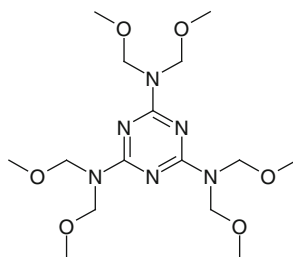
Benzyl-2-naphthylether
CAS No. 613-62-7



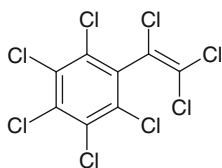
Methylbenz-iso-thiazole



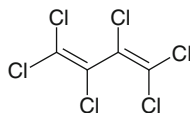
Bis-ethyl-iso-octanol lactone isomer



Hexamethoxymethylmelamine
CAS No. 68002-20-0



Octachlorostyrene
CAS No. 29082-74-4



Hexachlorobutadiene
CAS No. 87-68-3

Fig. 2.2 Chemical structures of potential industrial markers; These compounds do not occur in municipal sewage, their origin can be attributed to specific industrial production processes and they were detectable in industrial areas. They can be used to verify the input of specific industrial wastewaters to aquatic systems and to investigate the spatial distribution of the emission

2.4.1 *Chemical Characterization of Industrial Wastewaters and Toxicity Evaluation*

The approach includes toxicity tests with the whole wastewater, a chemical characterization of the samples and in most cases subsequent toxicity testing using reference materials of the identified compounds. Organic contaminants which were identified to contribute to the toxicity of whole wastewater samples are listed in Table 2.4.

The whole effluent toxicity of raw wastewaters from the *textile industry* was assessed using a bacterial biosensor and different luminescence inhibition assays. The EC₅₀ values of the polar compounds identified in the samples were determined with reference compounds and toxicity units were calculated. The results revealed that the identified polar compounds accounted for a significant portion of the total observed wastewater toxicity (Farré et al. 2001a, b). In a further comprehensive study on the chemical composition and toxicity of wastewaters from the textile industry and the receiving aquatic system in Brazil, the presence of three prevalent dyes came out. The combination of these dyes corresponded to a commercial product, which was also tested and exhibited mutagenic activity (Umbuzeiro et al. 2005).

Different chlorinated and brominated organic compounds were found in spent bleach liquor from the *pulp and paper industry* in Norway. The Ames test revealed mutagenic activity of the wastewater. Three halogenated organic compounds were found to be the main constituents of the wastewaters and were synthesized to investigate if these compounds were responsible for the observed effect. However, all three reference compounds only showed a weak mutagenic activity (Bjørseth et al. 1979; Carlberg et al. 1980). The authors noted that the compounds or the combination of compounds which were responsible for the mutagenic effect could not be identified.

Phenol, dihydroxybenzene and hydroquinone were present in the effluents of a treatment plant receiving wastewaters from a *chemical production site* in Italy. The toxicity of the effluent constituents was tested with a battery of experimental species and purchased reference compounds. The test results and data from the literature were used to calculate toxicity units. Effluent toxicity was under- or overestimated by calculating the sum of the toxicity units depending on which toxicity data and test organisms were used (Guerra 2001).

Toxicity tests with different industrial wastewaters from Sweden, Germany and Spain revealed the genotoxic and cytotoxic properties of untreated wastewaters from tanneries and from a chemical production site. The cytotoxic effects correlated with the presence of LAS in the samples (Castillo et al. 2001). The effluents of different industries in South China were tested for their acute toxicity with a battery of test species including green algae (*Pseudokirchneriella subcapitata*), daphnia, genetically modified strains of *Escherichia coli* and duckweed (*Lemna minor*) (Fang et al. 2012). In all effluents endocrine disrupting chemicals, PCBs, PAHs and PCDDs/PCDFs were detectable. Due to the complex chemical composition of the effluents, the authors remark that the observed toxicity of the effluents was caused

Table 2.4 Toxic organic contaminants identified in industrial wastewaters by chemical characterization and toxicity evaluation

Industry	Identified toxicant	Wastewater type	Approach	Experimental species	Biological effect	Reference
Textile industry	Alkylalcohol polyethoxylate, naphthalene sulfonates	Untreated wastewater	Toxicity tests with wastewaters, chemical characterization & toxicity tests with single reference compounds	<i>Escherichia coli</i>	Reduction of metabolic activity	Farré et al. (2001a)
	Alkylalcohol polyethoxylates, chlorophenols, phenol, nonylphenol polyethoxylate, polyethylene glycol	Untreated wastewater	Toxicity tests with wastewaters, chemical characterization & toxicity tests with single reference compounds	<i>Vibrio fischeri</i>	Luminescence inhibition	Farré et al. (2001b)
	Bromodinitrophenyldiazenyldipropenylaminomethoxyphenylacetamide (CI disperse Blue 373), dichloronitrophenylazoethylamilino] propionitrile (CI Disperse Orange 37), bromodinitrophenyldiazenyldiethylaminophenylacetamide (CI Disperse Violet 93)	Effluent	Toxicity tests with effluents, chemical characterization & toxicity tests with the industrial product	<i>Salmonella</i> strains	Mutagenicity	Umbuzeiro et al. (2005)
Tanneries	Octylphenol, nonylphenol, bisphenol A, estrone, estradiol, triclosan, PCBs, PAHs, PCDD/PCDF	Effluent	Toxicity tests with effluents & examination of wastewater constituents	Battery of different test species	Growth inhibition, mortality	Fang et al. (2012)
	LAS, polyethylene glycol, alkylalcohol polyethoxylates, nonylphenol polyethoxylate, benzene sulfonates, naphthalene sulfonates	Untreated wastewater	Toxicity tests with wastewaters & examination of wastewater constituents	<i>Vibrio fischeri</i> or <i>Photobacterium phosphoreum</i> , <i>Salmonella typhimurium</i>	Luminescence inhibition, mutagenicity	Castillo et al. (2001)

(continued)

Table 2.4 (continued)

Industry	Identified toxicant	Wastewater type	Approach	Experimental species	Biological effect	Reference
Pulp and paper industry	Trichlorotrihydroxybenzenes, bromomethylpropanylbenzene, dichloromethylpropanylbenzene	Spent bleach liquor	Toxicity tests with wastewaters, chemical characterization & toxicity tests with synthesized reference compounds	<i>Salmonella typhimurium</i>	Mutagenicity	Bjørseth et al. (1979) and Carlberg et al. (1980)
Chemical production sites						
Synthesized compounds not indicated	Octylphenol, nonylphenol, bisphenol A, estrone, estradiol, triclosan, PCBs, PAHs, PCDD/PCDF	Effluent	Toxicity tests with effluents & examination of wastewater constituents	Battery of different test species	Growth inhibition, mortality	Fang et al. (2012)
	Linear alkylbenzene sulfonates, benzene sulfonates, naphthalene sulfonates	Effluents	Toxicity tests with wastewaters & examination of wastewater constituents	<i>Vibrio fischeri</i> or <i>Photobacterium phosphoreum</i> , <i>Salmonella typhimurium</i>	Luminescence inhibition, mutagenicity	Castillo et al. (2001)
Synthesis of rubbers, fertilizers and industrial intermediates	Phenol, dihydroxybenzene, hydroquinone	Effluents	Toxicity tests with effluents, chemical characterization & toxicity tests with reference compounds	<i>Daphnia magna</i> , <i>Artemia salina</i> , <i>Brachionus plicatilis</i>	Mobility inhibition, mortality	Guerra (2001)
Coating industry	Octylphenol, nonylphenol, bisphenol A, estrone, estradiol, triclosan, PCBs, PAHs, PCDD/PCDF	Effluent	Toxicity tests with effluents & examination of wastewater constituents	Battery of different test species	Growth inhibition, mortality	Fang et al. (2012)

by a mixture of various substances which makes the identification of the causative constituents very difficult. Moreover, the mixture effects can be synergistic, additive or antagonistic. No further toxicity tests with reference compounds were conducted.

A review of approaches involving chemical analysis and toxicity testing of wastewaters and an overview of toxicity data for phenols, polyethoxylate surfactants, LAS, naphthalene and benzene sulphonates and other organic contaminants was presented by Farré and Barceló (2003). The study of the toxic response of these commonly in industrial wastewaters occurring compounds can help to identify their contribution to the total toxicity of wastewater samples. A broad-range correlation between presence of priority pollutants and whole effluent toxicity across a range of industry types was done by Sarakinos et al. (2000). There were effluent types for which there was one order of magnitude variation in inferred and measured toxicity. Overall, chemical-based assessments tended to overestimate toxicity of effluents containing high metal concentrations and to underestimate the toxicity of pulp mill effluents. Main and interaction effects of contaminants commonly found in textile dyes, pulp and paper mill effluents and oil refinery effluents were assessed by Parvez et al. (2008). Four-component mixtures using reference compounds were prepared and the toxicity of the different combinations were determined using a luminescence inhibition assay with *Vibrio fischeri*. In all tested mixtures, the magnitude of main effects was more significant than the interaction effects. It was furthermore highlighted that the behavior of an individual component changed in presence of other components. Specific physico-chemical properties, i.e. partition coefficient, molecular size and polarity of the compounds partly explained the behavior of the compounds in a mixture.

Although it was demonstrated that toxic effects correlated with the presence of specific contaminants in the investigated wastewater samples, the total toxicity of the samples could not be attributed to the identified compounds. This is due to the complex chemical composition of the samples, which impede a complete chemical characterization of the organic constituents. The presence of compounds which have not been considered as target analytes such as unidentified organic contaminants and heavy metals might also have contributed to the observed toxic activities. Furthermore, also other physico-chemical factors such as salinity, temperature, pH, nutrient concentrations and hardness might influence total wastewater toxicity.

2.4.2 Effects-Directed Analysis

This approach includes the extraction of wastewater samples and fractionation applying chromatographic methods such as HPLC and TLC. Subsequently, the obtained fractions are characterized according to their toxicity. The constituents of the toxic fractions are then analyzed by common analytical methods such as GC/MS, LC/MS and LC/MS-MS. As the last step, the toxicity of the identified compounds has to be confirmed (e.g. Schuetzle and Lewtas 1986; Brack 2003; Hewitt and Marvin 2005; Brack et al. 2008).

In the 1980s, the Environmental Protection Agency of the US developed a method for the extraction, fractionation and toxicity testing of unpolar organic contaminants in wastewaters (Burkhard and Ankley 1989; Burkhard et al. 1991). The sample extraction was executed with reversed phase SPE. The extracted compounds were eluted using mixtures of water and methanol. The toxicity of the obtained fractions was tested using *daphnia*. Only the toxic fractions were further separated with HPLC and analyzed with GC/MS. The crucial advantage of this newly developed method was the application of a reversed extraction phase. From this phase, the extracted compounds were eluted using relatively low toxic water–methanol solvent mixtures. The tolerance of most species towards methanol allows a testing of the fractions with up to one percent per volume methanol. Using this approach, effluent samples from the pharmaceutical industry, a textile factory and the pulp and paper industry were investigated and tested with *Vibrio fischeri* (Svenson et al. 1996). Further developments of effects-directed analysis allowed to augment the determinable compound spectrum to more polar and hydrophilic wastewater constituents (Fiehn and Jekel 1996; Fiehn et al. 1997; Reemtsma et al. 1999a, b; Castillo and Barceló 1999b; Reemtsma 2001). The exclusive usage of one test species probably leads to the systematic neglect of toxicants which do not have an effect on the specific cell metabolism of this test organism (Brack 2003). It is therefore a meaningful further methodological development to use a set of test organisms such as *daphnia*, green algae and luminous bacteria (Brack et al. 1999; Brack 2003). Additional to the conventional biotests also the genotoxic, hormonal and bioaccumulative potential of wastewaters should be evaluated (Pessala et al. 2004). The analytical methods applied for the effects-directed analysis of wastewater and field samples were reviewed in detail by Hewitt and Marvin (2005). Toxic organic compounds which were identified in industrial wastewaters applying effects-directed analysis are summarized in Table 2.5.

The acute toxicity of a **textile industry** effluent for *Vibrio fischeri* was found to be caused by two unsaturated fatty acids and two tridecanols, which accounted for 84 % of the toxicity of the effluent (Svenson et al. 1996). In the most toxic fractions of untreated textile wastewaters from Spain, a set of organic contaminants was identified including phthalic acid esters and nonylphenol isomers (Castillo and Barceló 2001). Different benzothiazole derivatives, cresol, dichlorobenzoic acid and methylbenzoic acid were identified as toxicants in **tanneries** effluents (Reemtsma et al. 1999a, b). In the toxic fractions of tannery wastewater, a variety of anionic and nonionic organic compounds were found. The confirmation step included toxicity tests with artificial water samples which contained the major identified contaminants in similar concentration levels (Castillo and Barceló 1999b).

A number of studies on the identification of toxicants in effluents from the **pulp and paper industry** have been conducted in Canada. Moreover, studies of the effects of pulp and paper mill effluents on aquatic organisms were reviewed in detail by

Table 2.5 Toxic organic contaminants identified in industrial wastewaters applying effects-directed analysis

Industry	Identified toxicant	Wastewater type	Experimental species	Biological effect	Reference
Textile industry	Linoleic acid, oleic acid, tridecanol, tridecanol isomer	Effluent	<i>Vibrio fischeri</i>	Luminescence inhibition	Svenson et al. (1996)
	Bis(ethylhexyl)phthalate, dibutylphthalate, nonylphenol isomers, nonylphenol ethoxylates, alcohol polyethoxylates	Untreated wastewater	<i>Daphnia magna</i>	Immobilisation	Castillo and Barceló (2001)
Tanneries	Thiocyanomethylthiobenzothiazole, mercaptobenzothiazole, Methylthiobenzothiazole	Tanyard wastewater	<i>Vibrio fischeri</i>	Luminescence inhibition	Reemtsma et al. (1999a, b)
	Cresol, dichlorobenzoic acid, methylbenzoic acid, methylthiobutyric acid	Beamhouse wastewater	<i>Vibrio fischeri</i>	Luminescence inhibition	Reemtsma et al. (1999a, b)
	Polyethylene glycol, nonylphenol polyethoxylate, alkylalcohol polyethoxylates, chlorocresol, pentachlorophenol, diethylphthalate, bis(ethylhexyl)phthalate, LAS, benzene sulfonates, naphthalene sulfonates	Untreated wastewater	<i>Vibrio fischeri</i>	Luminescence inhibition	Castillo and Barceló (1999b)
Pulp and paper industry	Trichlorocatechol, tetrachlorocatechol, dichlorohydroxyquinone	Effluent	<i>Salmonella</i>	Mortality	McKague (1981)
	Trichlorohydroxyfuranone	Effluent	<i>Salmonella typhimurium</i>	Mutagenicity	Holmborn et al. (1984)
	Octadecenoic acid amide, linoleic acid, linoleic acid isomer	Effluent	<i>Vibrio fischeri</i>	Luminescence inhibition	Svenson et al. (1996)
	Juvabione, dehydrojuvabione, manool	Effluent	<i>Oncorhynchus mykiss</i>	Hepatic mixed-function oxygenase activity	Martel et al. (1997)
	Chlorinated pterostilbene	Effluent	<i>Oncorhynchus mykiss</i>	Hepatic mixed-function oxygenase activity	Burnison et al. (1999)
	Methyl dehydroabietate, ethyl dehydroabietate, ethyl abietate, isopimaric acid, dehydroabietic acid, abietic acid	Effluent	<i>Saccharomyces cerevisiae</i>	Antiestrogenic activity	Terasaki et al. (2009)

(continued)

Table 2.5 (continued)

Industry	Identified toxicant	Wastewater type	Experimental species	Biological effect	Reference
Chemical production sites					
Synthesized compounds not indicated	Hydroxymethylthiobenzothiazole	Effluents	<i>Ceriodaphnia dubia</i> , <i>Pimephales promelas</i>	Mortality (96h-LC ₅₀)	Jop et al. (1991)
Synthesized compounds not indicated	Chlorobenzene, nitrobenzene, naphthalene, chloronitrobenzene, naphthol, aniline	Effluent	<i>Daphnia magna</i>	Mortality (24h- and 48h-LC ₅₀)	Yang et al. (1999)
Synthesized compounds not indicated	Benzopyrone, phenol	Effluent	<i>Daphnia magna</i>	Mortality (24h-LC ₅₀)	Jin et al. (1999)
Pharmaceutical industry	Phenylacetic acid methylester, substituted thiazol	Effluent	<i>Vibrio fischeri</i>	Luminescence inhibition	Svenson et al. (1996)

Hewitt et al. (2008) and Hewitt (2011). Chlorinated catechols were regularly detected in effluents from pulp mills and were found in water, sediment and fish bile (Tables 2.1 and 2.2). They were also identified as toxicants in chlorination-stage effluents from bleached kraft pulp mills (Table 2.5) (Mckague 1981). Another early study revealed that the mutagenicity of pulp mill effluents for *Salmonella* strains was mainly attributed to trichlorohydroxyfuranone (Holmborn et al. 1984). This compound is known to be performed as byproduct during the chlorination of humic acid (Meier et al. 1986). Effluents from the forest industry contained two unsaturated fatty acids and an unsaturated fatty acid amide as dominant toxicants, and almost the total toxicity of the sample (97 %) was accounted for by these three compounds with a contribution of the interaction of the three (Svenson et al. 1996). Effluents from a thermomechanical pulp mill induced hepatic mixed-function oxygenase activity in the rainbow trout. Organic compounds which naturally occur in the balsam fir *Abies balsamea* were identified as the constituents of the toxic fraction (Martel et al. 1997). Applying an effects-directed analytical approach, also chlorinated pterostilbene was identified as toxicant in pulp mill effluents. The presence of this compound corresponded with the induction of mixed-function oxygenase activity in the rainbow trout. Pterostilbene belongs to the pinosylvins family, a group of naturally occurring substances that are often present in coniferous trees (Burnison et al. 1999). Its chlorinated derivative is performed during the bleaching of the chemical pulp with chlorine. It is interesting that a biogenic compound, modified during bleaching, caused the observed biological response. Resin acids are the main constituents of natural tree resins. Despite their biogenic origin, it was demonstrated that several resin acids which occurred in paper mill effluents caused antiastrogenic effects (Terasaki et al. 2009).

Approximately 70 % of the toxicity of effluents from a **chemical production site** in the US was attributed to un-ionized ammonia. However, residual toxicity was assessed applying different fractionation and identification steps and revealed the presence of hydroxymethylthiobenzothiazole in the effluents (Jop et al. 1991). Several organic compounds were identified as the main toxicants in effluents from a chemical production site in China (Yang et al. 1999). A toxicity-based fractionation was also conducted with effluents from another chemical production site in China. A confirmation procedure using standard materials revealed that benzopyrone and phenol accounted for 44.6 % and 32.9 % of the whole effluent toxicity, respectively. It was observed that the two toxicants showed synergistic effects (Jin et al. 1999).

Phenylacetic acid methylester, an educt for the synthesis of pharmaceutical drugs and a substituted thiazol, which was a component of a pharmaceutical drug, were identified as main toxicants in the effluents of the **pharmaceutical industry** (Svenson et al. 1996).

The identification of wastewater constituents which are causing recorded toxic effects requires a lot of analytical expertise and has proven to be a “demanding challenge” (Hewitt and Marvin 2005). Although a number of good results were obtained during the early studies in the 1980s and 1990s, only few data were generated during the last decade.

2.5 Chemical Evaluation of Industrial Contamination Linked to Surveys of Environmental Impacts

We present here studies which attempt to correlate a detected industrial contamination in the environment with observed impacts on aquatic organisms. Studies which demonstrated that toxic effects in the field were directly attributed to the occurrence of specific industrial contaminants are discussed in Sect. 2.5.1. Surveys which revealed that the presence of industrial organic contaminants in field samples correlated with changes on the community level of aquatic organisms are discussed in Sect. 2.5.2.

2.5.1 Industrial Contamination and Toxicity Evaluation in the Field

Several studies demonstrated the toxic activity of field samples and related the observed effects to the presence of industrial organic contaminants. In the Nishitakase River, Japan, three mutagens were identified in water samples using *Salmonella typhimurium*. The compounds were identified as phenylbenzotriazole derivatives (Sect. 2.3, Table 2.2). The river is affected by discharges of the **textile industry** and because of the structural similarity it was postulated that the compounds are performed during industrial dyeing or during sewage treatment as metabolites of azo dyes (Nukaya et al. 1997; Oguri et al. 1998; Shiozawa et al. 2000). The mutagenic activity of water samples from the Cristais River, Brazil, for *Salmonella typhimurium* was also attributed to the impact of the textile industry (Umbuzeiro et al. 2004). The combination of three azo dyes, which was also present in the effluents and which corresponded to a commercial product, was identified (Sects. 2.3 and 2.4.1). The dyes were found to contribute to the mutagenic activity of the river water samples, and indirectly also an impact on the quality of the related drinking water was demonstrated. Coastal sediments from the vicinity of plants of the **petrochemical industry** in Kuwait were contaminated by heavy metals and PAHs. The fresh wet sediments were acutely toxic for *Vibrio fischeri*. The LC_{50} was negatively correlated with the PAH and heavy metal concentrations suggesting causality. However, no individual contaminant could be singled out as a main toxicant (Beg et al. 2001). Neoplasms and related disorders were found in fish from coastal waters close to a paper mill. Analysis of the sediments revealed the presence of 28 organic contaminants including resin acids, chlorinated phenols, chlorinated guaiacols and PAHs. Among the identified compounds, trichlorophenol, tetrachloroguaiacol, dehydroabietic acid, pyrene and fluoranthene revealed mutagenic activity in tests using *Bacillus subtilis* and *Salmonella typhimurium*. In liver samples of the spotted sea trout *Nibea mitsukurii* from the same area, the mutagen epoxystearic acid was identified (Kinae et al. 1981a, b). The Fenholloway River, US, receives effluents from a paper mill and contains populations of masculinized female eastern

mosquitofish *Gambusia holbrooki*. Water samples collected from the river and a control tributary were analysed. Fenholloway River water contained androstenedione. In the river sediments, androstenedione and progesterone were found. The authors concluded that pulp-derived phytosteroids are converted by microbes into progesterone and subsequently into androstenedione and other bioactive steroids. The presence of these compounds in the river might be responsible for the occurrence of the masculinized phenotype of female eastern mosquitofish (Jenkins et al. 2001, 2003). Sediments from a brook which received wastewaters from the chemical production site Bitterfeld were investigated. Bitterfeld was an important industrial production complex for chlorinated organic compounds in the former German Democratic Republic (Sect. 2.3). Organic toxicants were identified applying effects-directed analysis. Methyl parathion, prometryn, phenylnaphthalene amine, PAHs and tributyltin were confirmed as major toxicants using *Vibrio fischeri*, *Daphnia magna* and *Scenedesmus vacuolatus* (Brack et al. 1999).

Another type of studies applied caging experiments in areas affected by industrial discharges to assess whether the contamination had an effect on the exposed experimental species. The procedure included the identification of the causative toxicants. The toxicity of a leather **tannery** effluent to a transplanted population of blue mussels *Mytilus edulis* in an Irish estuary was assessed. Additionally, the mussels were exposed to single constituents of the effluents under laboratory conditions. After 1 year, the fitness of the transplanted mussels was at most sites comparable to the control group except those closest to the tannery outfall. The laboratory exposures revealed that the fungicide thiocyanomethylthiobenzothiazole induced lipid peroxidation in the digestive gland and amoebocyte proliferation in the gills (Walsh and O'Halloran 1997).

Rainbow trouts (*Salmo gairdneri*) were exposed for 48–144 h to effluents from a **paper mill** and were examined for the presence of dehydroabietic acid in the whole fish. Dehydroabietic acid concentrations in the exposed fish were 2–10 times higher than in the control group. The authors supposed that the accumulation of dehydroabietic acid could result in sublethal toxic effects (Fox et al. 1977). However, further toxicity tests to confirm this assumption were not carried out. In the blood plasma of caged rainbow trouts in Lake Saimaa, Finland, chlorinated phenols, chlorinated guaiacols, trichlorosyringol, tetrachlorocatechol and free resin acids were detected. In the control group, none of these compounds were detectable. The lake received bleached pulp mill effluents and the chlorinated contaminants were also present in the lake water (Table 2.2). During the 10-day caging period, increased haemoglobin and decreased plasma protein concentrations as well as a partial inhibition of liver UDP-glucuronosyltransferase was observed, even in a distance of up to 11 km from the source (Oikari et al. 1985). In whitefish *Coregonus lavaretus* exposed for 1 month in the same lake, chlorinated contaminant concentrations in bile and gut lipids correlated with distance from the source. The whitefish responded to the effluent exposure in a dose dependent way seen as a gradient change of the liver enzyme activity (Soimasuo et al. 1995). White sucker *Catostomus commersoni* was caged for 3 days in bleached pulp mill effluent and in a reference stream. The exposed group exhibited a 15–90 fold elevated mixed function oxygenase activity.

For the identification of the causative constituents, liver samples were extracted, fractionated and the fractions were tested for mixed function oxygenase activity in rat cells. Although PCDDs, PCDFs and chlorinated diphenylethers were identified in the toxic fractions, the respective concentrations were too low to be solely responsible for the whole observed effect (Parrott et al. 2000).

2.5.2 Industrial Contamination and Field Surveys of Ecological Changes

Studies on the relationship between chemical contamination and biological diversity in river systems were reviewed by Ricciardi et al. (2009). The authors noted that only a few studies couple chemical and biological analysis to evaluate water quality and the related effects on fluvial diversity. A response of freshwater invertebrates to chemical contamination was demonstrated (e.g. Cao et al. 1997; Day et al. 2006). A loss of sensitive species was observed at the most polluted sites along a pollution gradient in the River Trent, UK. Tolerant species were abundant at intermediately polluted sites and absent at clean sites (Cao et al. 1997). Interestingly, total individuals, total species and species richness of macroinvertebrates was highest near the outfall a sewage treatment plant in Louisiana, US, and declined further away (Day et al. 2006). The faunistic composition in coastal waters receiving sewage was also assessed (e.g. Inglis and Kross 2000; Wake 2005; Simboura et al. 1995; Bigot et al. 2006; Saunders et al. 2007; Calabretta and Oviatt 2008). Univariate and multivariate analysis revealed that the coastal area receiving sewage from Athens, Greece, could be divided into three zones which reflected the degree of pollution affecting the communities (Simboura et al. 1995). At stations closest to an urban center at the US coast, communities with opportunistic taxa were found which persisted in a state of low faunal diversity (Calabretta and Oviatt 2008). However, watershed analysis in these studies did not include a comprehensive characterization of the organic contamination but referred to heavy metal concentrations or standard parameters such as dissolved oxygen content, particulate organic carbon and nutrient concentrations.

In order to link contaminant exposure to community changes in fluvial systems, a biotic indicator of species at risk was developed and applied in different field studies in Europe and Australia (Schäfer et al. 2007, 2011; Liess et al. 2008). However, multivariate analysis of the contamination of floodplain sediments and community composition in a lake revealed that PAH concentrations did not correlate with changes of the benthic community (De Lange et al. 2009).

The occurrence of tributyltin in coastal waters was found to correlate with changes of the faunal composition of macrobenthos and meiobenthos (Warwick et al. 1990; Matthiessen and Law 2002), whereas oxygen depletion rather than chemical contamination was the dominant anthropogenic influence in an estuary receiving wastewaters (Saiz-Salinas 1997). In the San Francisco Estuary, US, many anthropogenic contaminants occurred at levels above known toxicity thresholds. A long term monitoring of associated effects on the estuary's plankton, fish, birds and

mammals revealed that no single contaminant was consistently related to effects among the biota considered. This was explained by the wide range of sensitivity to contaminants among the investigated organisms (Thompson et al. 2007). The Todos os Santos Bay in Brazil is a heavily industrialized area and urban center receiving discharges from an oil refinery. Macrobenthic communities in the bay are subject to chronic oil pollution which was documented by a chemical characterization of the sediments. The contamination correlated with a reduction in the number of species and diversity of benthic invertebrates (Venturini et al. 2008). Following the closure of major industries discharging into the Severn Estuary, UK, the concentrations of heavy metals, PCBs and PAHs were lower as compared to 25 years before. The long term monitoring indicated a recovery of faunal diversity in recent years implying that chemical contamination had been a forcing feature for the biota (Langston et al. 2010).

All mentioned studies compared faunal composition in contaminated areas to that in less impacted areas. In most cases, the contamination stemmed from mixed municipal/industrial sources and priority pollutants were considered to characterize the contamination. Ecological surveys of sites contaminated by industrial point sources combined with a comprehensive chemical characterization applying screening methods and toxicity evaluation are missing. Such an approach would be promising to understand the potential impacts of industrial contamination on aquatic diversity.

2.6 Conclusion

Major advancements in the identification of organic contaminants from industrial wastewaters include the development of new analytical techniques during the past decades which allow for the identification of previously unknown, emerging contaminants. Applying LC/MS techniques, polar wastewater constituents were identified which contribute to the whole effluent toxicity but are not detectable applying classical GC/MS methods. The successful application of GC/MS screening techniques led to the identification of structurally diverse organic contaminant groups which are educts, intermediates or byproducts of chemical syntheses conducted in different industrial branches. It enabled also the identification of contaminants which are performed during wastewater treatment and of contaminant metabolites, which might also pose a threat to the environment.

Studies tracing industrial contaminants in aquatic systems and examining the intrinsic underlying processes determining the fate of these compounds were applied. A simplified scheme is presented in Fig. 2.3. A marker concept has been developed by geochemists to understand the sources, transport and fate of organic compounds and was also applied to identify industrial markers.

The advancement of the analytical techniques and the identification of emerging contaminants rendered possible to evaluate the toxicity of these compounds and the potential impacts in the environment applying different toxicological approaches. The combination of chemical and toxicological methods allowed the identification

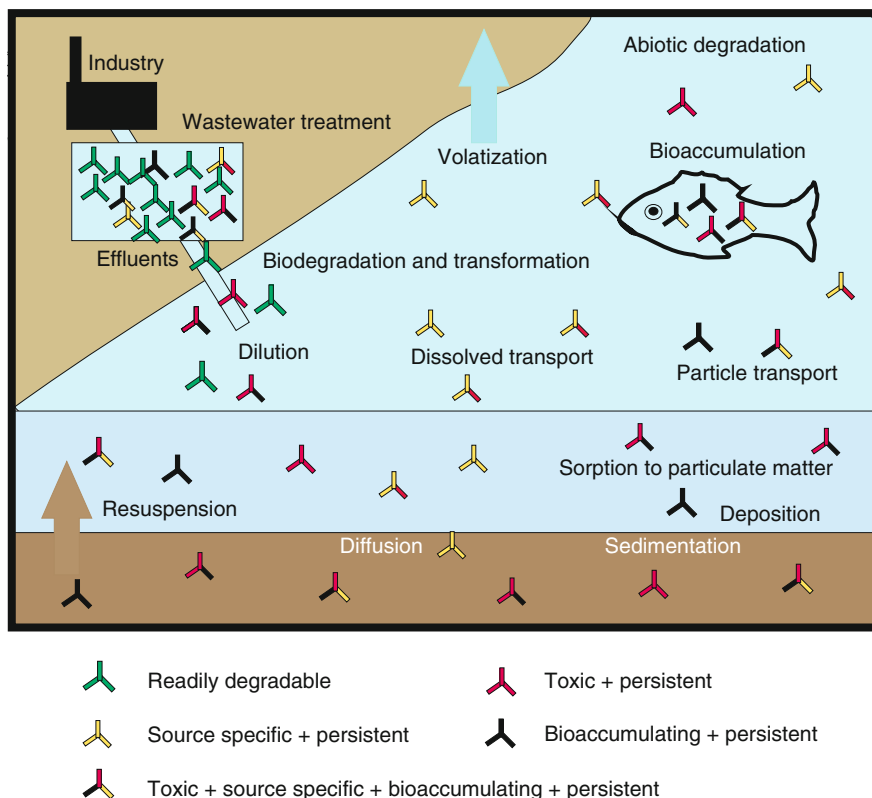


Fig. 2.3 Simplified scheme of the input and fate of industrial contaminants in river systems. The scheme shows the major processes controlling the environmental fate of contaminants which exhibit different physico-chemical properties

of organic constituents which contribute to the toxicity of industrial wastewaters. Toxic activities of different contaminant combinations were determined in order to assess main and interaction effects of contaminants commonly present in industrial wastewaters. The combination of chemical and biological investigations in the field is promising in order to assess the impact of chemical contamination on aquatic diversity.

Nevertheless, this review also shows that there are major gaps in our knowledge on the chemical composition of industrial effluents and their impact in the environment.

Numerous structurally diverse organic contaminants were identified in effluents from chemical production sites, the petrochemical and the pharmaceutical industry. Many of these compounds might be stable in aquatic systems, but as yet only limited attempts were made to trace these compounds in the environment. Only a few studies investigated effluents from other industrial facilities such as the food-processing industry, cement industry, automotive industry and

power stations. Information about the emissions of the coating and printing industry and of manufacturers of electric devices, toys and computers would be interesting, but are lacking.

The compound spectra found in field samples from industrialized areas was totally different from those in studies on effluents of the respective industries. This illustrates the complexity of the chemical composition of industrial wastewaters, even from the same industry types. It also shows the difficulty to generate comprehensive information on the chemical composition of industrial wastewaters. Only a limited number of studies focus beyond the identification of organic contaminants also on their fate in the hydrosphere.

Although organic constituents which contribute to the toxicity of industrial wastewaters were identified, the total toxicity of the samples could not be attributed completely to the identified compounds. Unidentified compounds, mixture effects and further physico-chemical factors impede the complete elucidation of the causes for the observed total toxicity. The toxicity of many organic compounds which were detected in industrial wastewaters and which are known to also occur in the environment is as yet unknown and they are not addressed by monitoring studies. Studies which investigate the impact of chemical contamination on aquatic diversity consider only priority pollutants such as PAHs, PCBs and organochlorine pesticides.

It has to be noted that the replacement of environmentally problematic compounds by novel industrial formulations is common but may lead to the presence of further, as yet unidentified contaminant groups in the effluents and in the hydrosphere with unknown impact in the environment. The number of registered substances is rapidly increasing, so does the number of potentially detectable organic contaminants in the environment. An example of an unidentified compound which has, according to the composition of the mass spectrum, at least three chlorine atoms is shown in Fig. 2.4. The compound was detected in effluent samples from a chemical production site.

Because industrial production sites are more and more shifted to emerging nations, such as China, India and Brazil, the use and contamination of water resources in these countries is increasing, but as yet only a few studies about these issues are available.

Research strategies which are in our opinion promising to address these gaps include:

- A comprehensive and industry branch specific chemical characterization of wastewaters, especially from chemical production sites, the petrochemical industry, the pharmaceutical industry and from so far neglected industry branches
- Examination of wastewater samples *and* field samples to assess the individual contamination profiles of industrialized areas
- An extended application of the organic marker concept in order to identify further industrial organic markers which are useful to verify the input of specific industrial wastewaters to aquatic systems, to investigate the spatial distribution of the emission and to disentangle different emission sources
- More information on the chemicals which are used for the different industrial production processes which is valuable for the identification of marker compounds

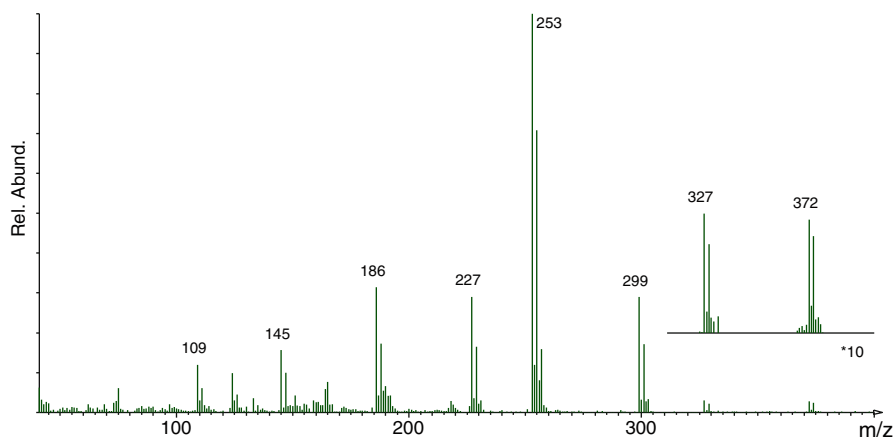


Fig. 2.4 Example of an unidentified compound which has, according to the composition of the mass spectrum, at least three chlorine atoms; The compound was detected in effluent samples from a chemical production site

- Further studies which combine chemical and toxicological methods to identify the constituents which are responsible for the toxicity of wastewaters
- Field studies combining chemical and ecological methods plus toxicity tests to assess the impact of industrial effluents on aquatic diversity
- More studies on industrial emissions and related impacts in emerging and developing nations in order to consider the geographical shift of industrial production

Chemical contamination was defined as a “planetary boundary” due to its global, ubiquitous impact on the physiological development of humans and other organisms with ultimate impacts on ecosystem structure/functions and because it acts as a slow variable affecting other planetary boundaries. Chemical contamination is one of the planetary boundaries, for which no boundary level could be determined. Setting of such a boundary would require knowledge of the critical impacts on organisms of exposure to 10,000 of chemicals and the related threshold concentrations, which is a gigantic task (Rockström et al. 2009). Industries emit a plentitude of structurally very heterogenic organic contaminants. Basic information on the chemical characteristics of these emissions is to some extent lacking but is necessary for the evaluation of associated risks and for the definition of thresholds.

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