2
Wastewater Characterization and Regulations

2.1
Volumetric Wastewater Production and Daily Changes

Wastewater is typically categorized into one of the following groups:

- Domestic wastewater (only produced in households).
- Municipal wastewater (domestic wastewater mixed with effluents from commercial and industrial works, pre-treated or not pre-treated).
- Commercial and industrial wastewater (pre-treated or not pre-treated).

Table 2.1 presents some average data for the Federal Republic of Germany.

Municipal wastewater is composed of 50% domestic wastewater on average. In some cities it may only amount to 25%, in other municipalities nearly 75%. This is of major significance, concerning the additional substances from certain factories which may be either non biodegradable or toxic. Commercial and industrial wastewater are treated together with domestic wastewater and rainwater in communities with a canal system (wastewater and rainwater). In particular, industrial plants with high water consumption have to treat their effluents in their own treatment plants. This is also required of many commercial and some agricultural works. In

Table 2.1 Total wastewater and municipal wastewater (Federal Republic of Germany, 60 million inhabitants, 248 534 km^2 area; from Pöpel 1997).

Total wastewater	**100%**	**$15.4 \cdot 10^9$ m^3 a^{-1}**	**694 L (inh. d)$^{-1}$**
Municipal wastewater	32	5.0	230
Industrial wastewater	47	7.2	320
Agricultural wastewater	1	0.2	7
Rainwater drainage in canals	20	3.0	137
Total municipal wastewater	**100%**	**$5.0 \cdot 10^9$ m^3 d^{-1}**	**230 L (inh. d)$^{-1}$**
Domestic wastewater	50	2.5	115
Rainwater	14	0.7	32
Commercial and industrial wastewater	36	1.8	83

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an increasing number of growing cities, domestic wastewater and rainwater are collected separately. Although the rainwater is often highly polluted by several organic and inorganic substances (from car washing, car accidents, high tides, etc.), it is mostly discharged untreated into rivers and canals.

Further information about the mean water consumption (= wastewater production) per inhabitant and per day in different European and North American cities is available (Chow et al. 1979; Pöppinghaus et al. 1994; Pöpel 1997). But we must be very careful when comparing these data, because sometimes they are valid only for one city and sometimes the data are valid only for domestic or for municipal wastewater, with or without rainwater. Therefore, we will not discuss these data here.

Within a 24-h period, the flow rate of domestic or municipal wastewater often changes by a factor of 3–4, causing a corresponding change in the flow rate at the treatment plants, because they most often have no storage tanks. Figure 2.1 shows a typical plot of flow rate versus time for a period of 24 h (Schuchardt 2005).

The minimum value during the night and the maximum at midday and evening are typical for many domestic and municipal treatment plants. In larger plants such as Berlin–Waßmannsdorf (~160 000 $m^3\ d^{-1}$), the profile of flow rate versus time is influenced by the length of the canal system.

The daily and weekly changes in the flow rate are given in Fig. 2.2 (Schuchardt 2005).

Typically, commercial and industrial wastewater flow rates have been published in relation to the mass of specific products (in $m^3\ d^{-1}$; Pöppinghaus et al. 1994; Henze et al. 2002). We will not consider these data here; however, see Section 2.4 where relevant regulations are discussed.

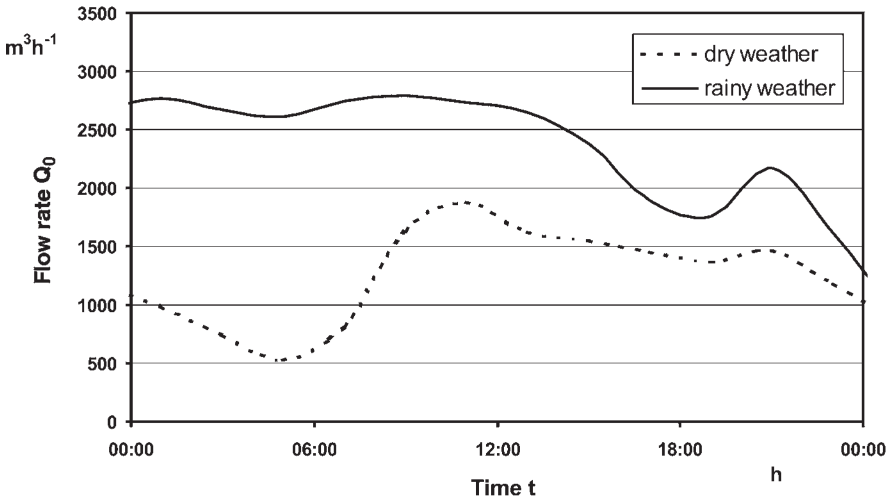

Fig. 2.1 Daily change in flow rate at the municipal WWTP Waßmannsdorf, near Berlin, BB 12 (basin 12), Q_o from on-line measurements (Schuchardt 2005). Dry weather 6 September 2001; rainy weather 10 September 2001.

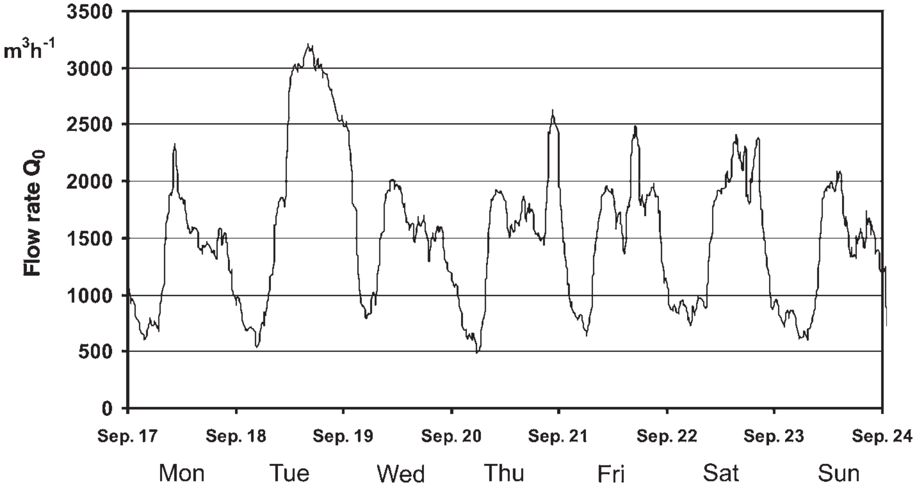

Fig. 2.2 Daily and weekly change in flow rate at the municipal WWTP Waßmannsdorf, near Berlin, BB 11 (basin 11), 17–24 September 2001, Q_0 from on-line measurements.

2.2 Pollutants

2.2.1 Survey

All wastewater classes (domestic, municipal, commercial or industrial) contain the following groups of pollutants:

1. Dissolved substances

a) Organic materials
- biodegradable substances
- non-biodegradable substances

b) Inorganic materials
- nutrients, used in part or totally by microorganisms
- metal and heavy metal ions, used often only in very small amounts by microorganisms as trace elements (often toxic in slightly higher concentrations)

2. Colloids

a) Non-settleable small drops of oil and grease

b) Organic and inorganic small solid particles

3. Suspended solids

a) Organic particles
   - microorganisms (bacteria, viruses, worm eggs, protozoa), mostly non-settleable
   - other organic materials (residual particles from fruits, vegetables, meat, etc.), mostly settleable

b) Inorganic particles
   - sand, clay, minerals
   - partly organic and partly inorganic particles

2.2.2 Dissolved Substances

2.2.2.1 Organic Substances

The sum of all the different dissolved organic molecules in domestic wastewater can be approximately characterized by the average molecular composition $C_{18}H_{19}O_9N$ (Pöpel 1997) with a mass of 393 g mol^{-1}.

The concentration can be measured by chemical oxidation using potassium dichromate. For complete oxidation, the necessary oxygen and the carbon oxidized, measured as CO_2, can be calculated from:

$$C_{18}H_{19}O_9N + 17.5\ O_2 + H^+ \rightarrow 18\ CO_2 + 8\ H_2O + NH_4^+ \tag{2.1}$$

For wastewater with 1 mol m^{-3} $C_{18}H_{19}O_9N$ (or 393 g m^{-3}), $17.5 \cdot 32 = 560$ g m^{-3} O_2 is needed and $18 \cdot 12 = 216$ g m^{-3} CO_2-C is produced.

Therefore, the oxygen consumed and the CO_2-C produced can be used as characteristics of the concentration, resulting in:

$S_{th} = 560$ g m^{-3} COD (*c*hemical *o*xygen *d*emand)

or

$S_{th} = 216$ g m^{-3} DOC (*d*issolved *o*rganic *c*arbon)

for

$S_{th} = 393$ g m^{-3} substrate

The theoretical value $S_{th} = 560$ g m^{-3} COD would only be measured for a total oxidation according to Eq. (2.1). Usually, a part of the oxidized mean products cannot be completely oxidized using the standard test. If a rapid test is used, the measured COD is even lower than that of the standard test (Section 2.3.2). For the theoretical value, the standard value would follow as:

$S_{St} = 0.83 \cdot S_{th} = 465$ g m^{-3} COD

giving a rapid test value of only:

$S_{rt} = 0.70 \cdot S_{th} = 392$ g m^{-3} COD (Ramalko 1983)

The oxygen used for biological CO_2 and H_2O formation as well as for bacterial growth during a 5-day batch process (Henze et al. 2002; Table 2.1) for this theoretical domestic wastewater is:

$S = 280\ g\ m^{-3}$ BOD_5 (*b*iochemical *o*xygen *d*emand over 5 days without nitrification).

The BOD_5 is always lower than the COD, although bacteria use oxygen not only for CO_2 and H_2O production, but also for growth. We can attribute this to several reasons:

- Only a part of the organics in the wastewater can be used by the bacteria as a carbon and energy source.
- Some substances can only be partly used. Some products of metabolism are excreted.
- Bacteria die and form lysis products, which can only be used in part by living bacteria.
- After 5 days, some biodegradable substances are still left. Therefore, occasionally BOD_{10} or BOD_{20} are used.

The COD and DOC of pure organic substances can be calculated in the same way as shown above, giving the theoretical COD S_{th}. Again, the measured values S_{st} and S_{rt} are lower for the reasons mentioned above. Some data have been published for a number of chemicals often used in chemical industry (Busse 1975; Pöppinghaus et al. 1994).

Of more practical importance are the dissolved organics from the processing water of specific products. Mostly, they consist of thousands of specific compounds, as discussed above for domestic wastewater. Table 2.2 presents data on the substrate concentration S measured as COD and BOD_5 in processing water from the food industry. Usually the standard method is used to measure COD.

In most cases, the concentrations of COD and BOD_5 are considerably higher than in domestic or municipal effluents. Therefore, anaerobic wastewater treatment processes are often preferred. This is also true for effluents from the brewing

Table 2.2 Some typical concentrations of wastewater from the food industry (Lehr- und Handbuch der Abwassertechnik 1985).

Product	S ($mg\ L^{-1}$ COD)	S ($mg\ L^{-1}$ BOD_5)
Sugar	7500	5000
Maize starch	17608	11543
Potato starch	7416	6333
Wheat starch		12344–18270
Rice starch	2192	1475
Margarine	1000–2000	500–1000
Vegetable refinement		5000–8000
Fruit juice	300–800	25–1380
Slaughterhouse	2579–6650	1900
Fish processing		1530–2567

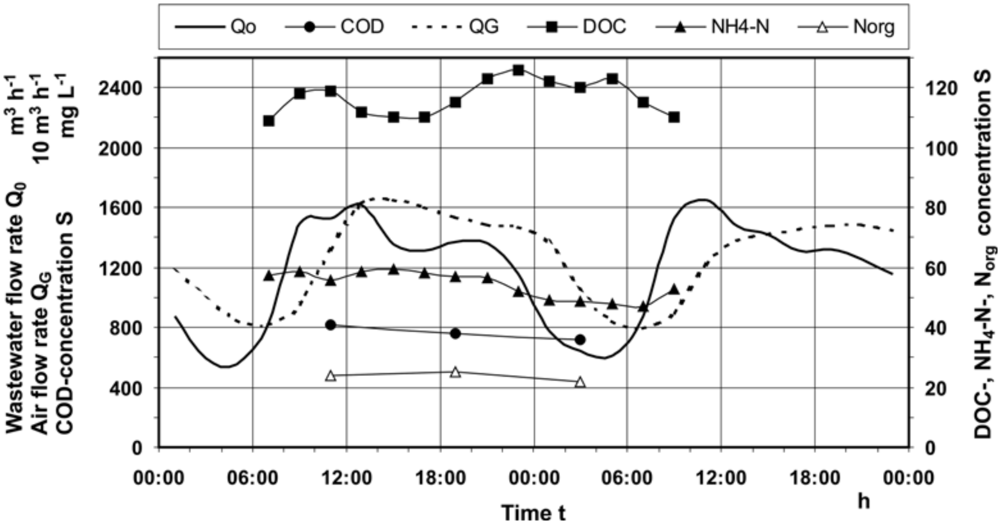

Fig. 2.3 Daily change in flow rate and concentrations (● COD, ■ DOC, ▲ NH_4-N, △ N_{org}) at the municipal WWTP Waßmannsdorf, near Berlin, BB 12 (basin 12), 14/15 November 2001, Q_0 from on-line measurements, concentrations from 2 h mixed samples.

industry (Lehr- und Handbuch der Abwassertechnik 1985). Wastewater with high loads of organics must be treated separately in other industries such as the chemical industry, oil refineries, paper and cellulose production and the pharmaceutical industry (Lehr- und Handbuch der Abwassertechnik 1985).

In contrast to the flow rate, the concentrations of organics are nearly constant over a 24-h period (Fig. 2.3).

Therefore, the changes in load at municipal treatment plants are defined approximately by their change in flow rate. In contrast, the change in the loads from industries can differ remarkably from the changes in flow rate.

2.2.2.2 **Inorganic Substances**

The most important dissolved inorganic substances are nutrients, metals and heavy metals.

Nutrients

Special attention is given to nitrogen and phosphorus compounds which cause the growth of cyanobacteria and microalgae in lakes, rivers and the sea (eutrophication; see Chapter 10). The main dissolved components and their concentrations in municipal wastewater are presented in Table 2.3.

Table 2.3 Typical content of dissolved nitrogen and phosphorus compounds in municipal wastewater (in mg L^{-1}; Henze et al. 2002).

Nutrient	Concentration	Strong	Medium	Weak
Nitrogen	S_{NH}, $NH_3 + NH_4$	50	25	12
	S_{ND}, organic N.	35	15	8
Phosphorus	S_{PO4}, orthophosphate	8	4	2
	$S_{org.P}$, organic	5	3	1
	S_{PP}, inorganic	10	5	3

Dissolved $NH_3 + NH_4$ values for industry and agriculture are given in Table 2.4 (Dombrowski et al. 1989). These concentrations are considerably higher than those for municipal wastewater, resulting in more difficult processing and higher costs.

Higher phosphorus concentrations are observed most frequently in effluents of the fertilizer industry, with up to $S_{PO4} = 50$ mg L^{-1} P.

Table 2.4 Typical content of nitrogen (NH_3-N + NH_4-N) in wastewater from industry and agriculture (Dombrowski et al. 1989).

Industry	S_{NH} (mg L^{-1})	Agriculture	S_{NH} (mg L^{-1})
Coke ovens	800–1000	Slaughter houses	80
Coal gasification	5–1000	Intensive livestock farming	
Oil refineries	23.8–752.0	Swine	2300
Fertilizer	200–940	Cattle	500–2300
Glass	196	Utilization of animal carcasses	807
Cellulose and paper	264		

Heavy Metals

Some heavy metals are important trace elements and necessary for bacterial growth because they are components of some enzymes and other proteins. However, municipal and industrial wastewater contain much higher concentrations. Therefore, their concentrations must be limited by law, so that they are not enriched in the food chain of animals.

Concentrations vary greatly in both municipal and industrial effluents. Therefore, it is senseless to publish areas of different values here. We will come back to this point in Section 2.4.2.

2.2.3
Colloids

A colloid is a suspension of small particles, mostly in water. These particles may be small solids and small oil droplets or other liquids insoluble in water. In the latter case, the colloid is called an emulsion. Water-in-oil (fat) emulsions (creams, butter, etc.) are of great practical importance. We must often treat oil-in-water emulsions or solid-in-water colloids (turbid water) as impurities in the environment. Both will be described shortly in this section.

2.2.3.1 Oil-In-Water Emulsions

Part of the oil added to water is suspended as large droplets, which rise to the water surface and form an oil film. Another part forms very small droplets as a result of energy input, for example from a rotating stirrer, and is not able to rise to the surface because of the equilibrium between very low buoyancy forces and downward diffusion. They behave as large molecules and move very slowly. If they collide with other small droplets, they coalesce; and then the diameter of the droplets increases and the emulsion is destabilized.

A stabilized emulsion arises by adsorption of anions at the surface. These anions may already be dissolved as SO_4^{2-}, HCO_3^-, Cl^-, etc., or they may be added as special chemical compounds (emulsifiers). The following results are obtained by experiments with dodecane (not soluble in water) and the emulsifier Eumulgin ET 5 (Henkel AG). In a rotor–stator mixer at a speed of 10000 min^{-1} and a stirring time of 60 s, a stable emulsion was produced with the droplet size distribution presented in Fig. 2.4.

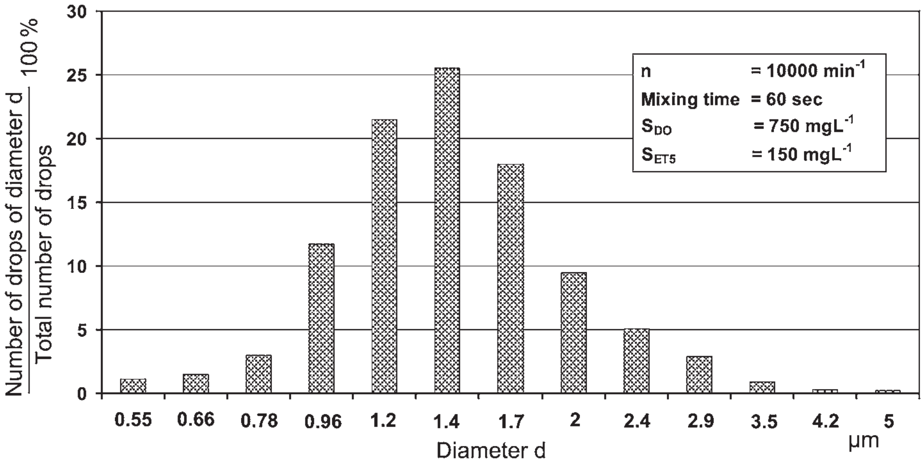

Fig. 2.4 Size distribution of dodecane droplets in an emulsion stabilized by an emulsifier (Eumulgin ET 5), S_{DO} = 750 mg L^{-1}, stirrer speed n = 10000 min^{-1}, c_{ET5} = 150 mg L^{-1}, mixing time = 60 s (Cuno 1996).

The diameters of the droplets were measured and the droplets were counted using a microscope (Cuno 1996). In this emulsion, nearly all droplets had diameters between 0.5 μm and 3.5 μm, with a maximum fraction of 25% at 1.5 μm. The fraction describes the number of droplets of this size related to the total number.

Table 2.5 presents some industrial effluents with different oil concentrations. Only a part of the oil concentrations mentioned is really emulsified, while a part is suspended as larger droplets and yet another part may exist as an oil film at the surface.

Table 2.5 Industrial oil/water suspensions and emulsions (Patterson 1985).

Wastewater production	Oil concentration ($mg\ L^{-1}$ COD)
Steel rolling mill	7200
Aluminium rolling mill	5000–50 000
Ferrous casting	20–716
Food industry	3820
Fish processing	520–13 700
Production of vegetable oil	4000–6000
Washing water of airplanes	500–12 000
Textile industry (cleaning of wool and threads)	1605–12 260

It is difficult to measure the concentration of emulsified oil. After separation of nearly all the suspended oil particles by sedimentation (ascending), the oil in the stabilized emulsion can be oxidized and measured as total oxygen demand (TOD), or COD for longer oxidation times. But if there are other dissolved organics, the emulsion must be separated in advance using nano- or ultrafiltration membrane or an extraction method (direct extraction with petrol ether; DIN 38409; Walter 1993).

2.2.3.2 **Solid-In-Water Colloids**

Small solid particles (minerals, silt, organics, microorganisms) form stabilized colloids after they have adsorbed anions. The light incident on a particle is not transmitted, it is reflected. Depending on the concentration, the mean particle diameter, and particle distribution, turbidity can be observed and measured by using one of two methods: turbidimetry and nephelometry. The latter is widely used. A light beam is directed into the water sample and the light is scattered by the particles (Tyndall effect) and converted to a galvanometric reading. This is compared with a standard such as a formazine polymer colloid (1.25 $mg\ L^{-1}$ hydrazine sulfate and 12.5 $mg\ L^{-1}$ hexamethylenetetramine) and set as 1 FTU (*f*ormazine *t*urbidity *u*nit). The colloid standard is used because of its stability and reproducibility (Bratby 1980).

In addition to colloidal solid particles in water, the predominant group of solids is mostly non-settleable. These can be removed by porous membrane filtration of the total solids (TS) sample (pore size: Denmark, 1.6 μm; Germany, 0.45 μm; Henze et al. 2002). The TS are now separated into a more defined solid-in-water colloid, often called “dissolved solids”, and a fraction of suspended solids.

2.2.4 Suspended Solids

Unfortunately, in most practical cases, colloids are not separated from suspended solids. Using a graduated Imhoff cone, a sedimentation test yields two fractions: (a) the settleable solids below and (b) the non-settleable solids above, the fraction which now contains the colloid particles.

Mostly, only the settleable solids are measured as X (in mL L^{-1}) by reading the scale on the lower part of the Imhoff funnel. More exact data are obtained after separation of the two portions. The organic mass and inorganic mass are definable after filtration, drying, weighing, incineration at 500 °C and re-weighing the ash. Table 2.6 presents some typical data for domestic wastewater.

Table 2.6 Suspended solids as organics and minerals (Pöpel 1997), Q = 115 L (inh. d)$^{-1}$ (Table 2.1; selected and partly converted data).

Solids	Unit	Settleable solids	Non-settleable solids	Total
Organics	g MLVSS d^{-1}	40	20	60
	g L^{-1} MLVSS	0.350	0.175	0.525
Minerals	g MLSS d^{-1}	20	10	30
	g L^{-1} MLSS	0.175	0.086	0.260

In municipal wastewater and especially in industrial effluent, the concentration of suspended solids can vary considerably from the data in Table 2.6. For more specific information about different branches of industry, see Pöppinghaus et al. (1994).

2.3 Methods for Measuring Dissolved Organic Substances as Total Parameters

2.3.1 Biochemical Oxygen Demand

The biochemical oxygen demand (BOD_n) is the mass of oxygen which is needed by microorganisms during a test in closed flasks over a period of 5 (BOD_5), 10 (BOD_{10}) or 20 days (BOD_{20}) at a temperature of 20 °C, pH 7–8 and after the addition of nutrients. Additional bacteria have to be injected into samples which contain too few bacteria. In these cases, biologically treated wastewater or contaminated surface water can be added to domestic wastewater after settling. The BOD_5 of these supplements must be taken into account (Fresenius et al. 1988).

Depending on the concentration of biodegradable substances, it may be necessary to dilute with water containing various nutrients. Four different solutions with special nutrients should be prepared, which can be used simultaneously as dilution water. This should be saturated with oxygen.

Predominately, two different methods are used to measure the amount of oxygen needed. The quantity of dissolved oxygen consumed is determined by measuring the difference of dissolved oxygen, either electrometrically using an electrode or manometrically (Ramalko 1983; Fresenius et al. 1988).

In the first case, glass flasks of 110–130 ml or 250–300 ml (with stoppers) are prescribed, which must be totally filled after they are diluted accordingly with water.

In the second case, the sample is put into a vessel leaving a space for air, which can be closed off from the atmosphere. The sample must be stirred or shaken during the measurement in order to avoid any influence of mass transfer on the O_2 consumption rate. The CO_2 produced, which is not dissolved or converted to HCO_3^-, is adsorbed by potassium hydroxide. According to the volume of the air enclosed in the bottle, a certain amount of oxygen is available, so that higher dilutions are not necessary.

Usually, BOD measurements are made after removing the settleable solids from the sample by sedimentation. Therefore, the measurement includes not only the dissolved organics but also the organic colloids and the non-settleable solids, which may partly be hydrolyzed and used by aerobic microorganisms. In addition, bacteria use oxygen by endogenous respiration; and some of them die and thus produce new substrate after cell lysis. The most important disadvantage of the method, however, is its long measuring time. BOD_5 is not suitable as a control parameter for treatment plants if rapid measurements are necessary.

Several rapid BOD measuring devices have been developed to improve response time. The ZAW-LAB and ZAW-FIX (GIMAT) are semi-continuous analyzers for the on-line determination of respirometry rates. A sample is saturated with oxygen and mixed with an adapted culture. The oxygen consumption rate is determined from the sinking dissolved oxygen concentration over time and is used for the calculation of the BOD_5. The Bio Monitor from LAR (Laser and Analytical Research GmbH) works continuously. Two small, four-step cascades are operated in parallel. One is supplied with air, activated sludge and sample, and another only with air and activated sludge. After a retention time of only 1–4 h, the substrate is nearly completely consumed, resulting in a corresponding oxygen consumption, which is calculated from the difference between the two cascades. The short measuring time results from the elevated temperature of 30–35 °C and the higher bacterial concentration.

2.3.2
Chemical Oxygen Demand

The chemical oxygen demand (COD) is defined as the mass of oxygen needed for the complete oxidation of an organic compound present in water. For the oxidation of glucose $(CH_2O)_6$, a representative hydrocarbon, 1 mol O_2 mol^{-1} C is needed according to:

$$(COH_2)_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O \tag{2.2}$$

For the standard COD test, a measured sample with a known excess of potassium dichromate ($K_2Cr_2O_7$) is mixed after the addition of H_2SO_4 and silver sulfate (Ag_2SO_4). The organic matter is oxidized over a 2-h heating period. After this time, the concentration of the remaining dichromate is measured by titration with ferroxine (Fe^{2+}) (Ramalko 1983; Fresenius et al. 1988):

$$Cr_2O_7^{2-} + 6\ e^- + 14\ H^+ \rightarrow 2\ Cr^{3+} + 7\ H_2O \tag{2.3}$$

$$Cr_2O_7^{2-} + 6\ Fe^{2+} + 14\ H^+ \rightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O \tag{2.4}$$

Equation (2.3) is a reduction reaction, because of the use of electrons. The complete oxidation of glucose is expressed by:

$$(COH_2)_6 + 6\ H_2O \rightarrow 6\ CO_2 + 24\ H^+ + 24\ e^- \tag{2.5}$$

After combining (2.3) and (2.5) we obtain:

$$(COH_2)_6 + 4\ Cr_2O_7^{2-} + 32\ H^+ \rightarrow 6\ CO_2 + 8\ Cr^{3+} + 22\ H_2O \tag{2.6}$$

Four moles of $Cr_2O_7^{2-}$ are needed for the oxidation of six C atoms.

In this special case, all of the carbon in the organic compound is assumed to be oxidized and the COD can be called TOD (total oxygen demand). Usually, the substrate is only partly oxidized by $K_2Cr_2O_7$ and some organic oxidized products remain. These values of the COD may vary between 70% and 95% of the TOD.

In order to reduce the 2 h needed for this measurement, several instruments have been developed and automated. In the on-line continuous COD measurement device made by the company Product Finder the standard method includes mixing the heated sample with $K_2Cr_2O_7$ to drive a reduction of Cr(VI) to Cr(III). The green coloration is measured colorimetrically and is proportional to the amount of Cr(III) formed and the concentration of oxidized organic substance.

Other oxidants are used by other developers. LAR takes advantage of OH° radicals which oxidize the organics at a high rate. These radicals are produced by an electrode, with a rate proportional to the electrical current and therefore the rate of oxidation. Other instruments use the fast oxidation of H_2O_2/UV with the measurement of H_2O_2 consumption (GIMAT), or O_3 consumption with the measurement of O_3 in water (PHOENIX-1010 STIP; Isco Inc.) or in air (OXI-JET; UVT-Ingenieurbüro für Umwelt- und Verfahrenstechnik).

2.3.3
Total and Dissolved Organic Carbon

Organic substances contained in water samples are oxidized either (a) by UV rays (low-pressure UV lamp) in the water sample, (b) by wet chemical oxidizers in the water sample, or (c) by oxidizing at high temperatures (~950 °C) with or without catalysts.

The amount of CO_2 can then be measured, either (a) by using a non-dispersive CO_2 infrared analysis device, or (b) by using a flame ionization detector (FID) after conversion of CO_2 into CH_4 by heterogeneous catalysis.

TOC (total organic carbon) measurement is usually performed on the sample after sedimentation.

If the DOC (dissolved organic carbon) should be measured, the sample has to be separated from suspended non-settleable particles and from some colloids, by using a glass fiber filter or a centrifuge (Fresenius et al. 1988). Both filters and centrifuge glasses must be cleaned carefully with distilled water in advance.

The TC (total carbon) is the sum of organic and inorganic carbon (CO_2, HCO_3^-, CO_3^{2-} dissolved in water). Often both the organic and the inorganic carbon are measured after heating the sample to 950 °C (reaction tube 1, TC) and only the inorganic carbon at 150 °C (reaction tube 2, TC-TOC). The difference between TC and inorganic carbon is the TOC, if the sample was not filtered, and is equal to the DOC if the sample was filtered (Ramalko 1983).

The measurement of TOC/DOC has been automated since and the time for analysis reduced remarkably. In the Shimadzu TOC-4110, the sample is oxidized catalytically after heating and CO_2 is measured by low-pressure infrared analysis.

Table 2.7 Total concentration parameters for typical raw domestic wastewater and after biological treatment with nitrification (Henze et al. 1995).

Parameter	Unit	Wastewater	
		Raw	After treatment
Biochemical oxygen demand			
• after 5 days	mg L^{-1} BOD_5	280	25
• after 20 days (total)	mg L^{-1} BOD_{20}	400	35
Chemical oxygen demand	mg L^{-1} COD		
• easily biodegradable		60	5
• slowly biodegradable		200	10
• with $KMnO_4$		180	30
• with $K_2Cr_2O_7$		600	100
• total (900 °C, Pt catalyst)		800	230
Total organic carbon	mg L^{-1} TOC		
• at 800 °C		200	35
Dissolved organic carbon	mg L^{-1} DOC	160[a)]	15[a)]

[a)] WWTP Waßmannsdorf, near Berlin.

The sample is diluted and prepared automatically, resulting in a low measuring time of 3–5 min. In two other developments, the combustion temperature is increased to 1150 °C (TOC-/TC-Analyzer; GIMAT) or to more than 1200 °C (Quick TOC; LAR) without using a catalyst. In all cases, calibration is necessary. Frequently, potassiumhydrogenphthalate is recommended (Fresenius et al. 1988).

Table 2.7 presents some data for total concentration parameters in a typical domestic wastewater.

Several points are worth highlighting:

- The BOD_5 is lower than the BOD_{20} because of nitrification, which starts only after several days, and because of the removal of slowly biodegradable substances (see Section 2.3.1).
- The COD depends strongly on the method used. A total oxidation and conversion to CO_2, H_2O, NO_3^- is only possible by combustion at 900 °C and by using a catalyst or at ~1200 °C without any catalyst.

2.4 Legislation

2.4.1 Preface

German legislation concerning the discharge of wastewater into public sewers (Ind. VO 1989: Indirekteinleiterverordnung; regulation of indirect introduction) and into surface waters (Mindestanforderungen nach §7a, WHG (2002); minimum requirement, §7a, water resource policy law) places a limit on emissions. This will be presented shortly in the next section.

After that we will briefly discuss EU guidelines for pollution control of waters, which limit immissions, that is, for discharges of treated wastewater into water, not concerning fixed loads or concentrations, but loads which can still be tolerated by the water.

2.4.2 German Legislation

2.4.2.1 Legislation Concerning Discharge into Public Sewers

The most important piece of legislation is the "Indirekteinleiterverordnungen der Bundesländer der Bundesrepublik Deutschland (Ind. VO 1989)", regulation of indirect introduction by the states of the Federal Republic of Germany. All industries with discharges of contaminants into public sewer systems which exceed a minimum concentration or hourly load must report this to the local water authority. Effluents with high concentrations and loads coming from specific origins must be treated before being discharged into the public sewers. The Ind. VO of Baden Württemberg (regulation of indirect water disposal for Baden Württemberg, Germany) is presented as an example (Table 2.8).

Table 2.8 Threshold values required for approval to discharge hazardous materials into public sewer systems (Ind. VO Baden Württemberg; WEKA 2005).

Material or group of materials	Method of analysis	Thresholds	
		Concentration (mg L^{-1})	Load (g h^{-1})[a]
Cl total	DIN 38 408-G 4-1/2, June 1984	0.2	4.0
Cyanide	DIN 38 405-D 13-2, Feb. 1981	0.1	2.0
As	DIN 38 405-D 18, Sept. 1985	0.05	1.0
Pb	DIN 38 406-E 6, May 1981	0.2	8.0
Cd	DIN 38 406-E 19, July 1980	0.02	0.4
Cr total	DIN 38 406-E 22, March 1988	0.2	8.0
Cu	DIN 38 406-E 22, March 1988	0.3	12.0
Ni	DIN 38 406-E 22, March 1988	0.2	6.0
Hg	DIN 38 406-E 12-3, July 1980	0.005	0.1
Ag	DIN 38 406-E 22, March 1988	0.1	6.0
Zn	DIN 38 408-E 22, March 1988	0.5	20.0
Halogenated hydrocarbon AOX	DIN 38 409-H 18	0.5	10.0
1,1,1-trichloroethane, trichloroethene, tetrachloroethene, trichloroethane	Gas chromatography	0.1 (Cited values are the sum of all mentioned compounds, calculated as Cl)	2.0

a) Thresholds in g h^{-1} must be taken from water volume within 1 h.

Several other problems may arise after a discharge of industrial effluents into the public sewer system. Here, only a few are mentioned:

- The settling rate of some solid particles with low density is not sufficient.
- Toxic compounds may decrease the biological activity of bacteria.
- High water temperature may cause an increase of total water temperature to >35 °C and the metabolism of bacteria may be slowed or stopped.
- High, isolated loads of industrial discharges may cause too high a loading of the municipal plant, resulting in non-conformance to the regulations.

In these cases, buffer tanks are often prescribed to protect the treatment processes of the municipal plant. Guidelines are given with ATV-A 115.

2.4.2.2 Legislation Concerning Discharge into Waters

These limiting emission values are valid for effluents from wastewater treatment plants and canals into bodies of water. Naturally, these canals collect treated wastewater from municipalities and industries, but other sources of wastewater may be additionally polluted by agriculture or small communities.

Table 2.9 AbwV, Appendix 1: municipalities.

Minimum requirements after §7a, WHG (2002), Appendix 1 (kg BOD_5 d^{-1})	S_S (mg L^{-1} COD)	S_S (mg L^{-1} BOD_5)	$S_{NH4\text{-}N}$ (mg L^{-1} N)	S_{Nt} (mg L^{-1} N)	S_{Pt} (mg L^{-1} P)
Class 1: <60	150	40	–	–	–
Class 2: 60–300	110	25	–	–	–
Class 3: 300–600	90	20	10	–	–
Class 4: 600–6000	90	20	10	18	2
Class 5: >6000	75	15	10	13	1

Table 2.10 AbwV, Appendix 47: washing water for fuel gas from power plants.

Minimum requirements (after §7a, WHG 2002)	Appendix 47: power plants		
Specific concentration (mg L^{-1})	**Coal (mg kg^{-1} chloride; Cl^-)**	**Lignite coal (mg kg^{-1} Cl^- content at <0.05 mass%)**	**Domestic refuse (mg t^{-1} waste)[d]**
COD	80[a] 150[b]	80[a] 150[b]	
Filterable material	30.0	30.0	
Pb	3.6	0.2[c]	30
Cd	1.8	0.1	15
Cr, total	1.8	1.0	150
Cu	18.0	1.0	150
Ni	18.0	1.0	150
Hg	1.8	0.1	15
Zn	36.0	2.0	300
F	30.0	30.0	

a) Using slaked lime.
b) Using limestone.
c) Loads given in g h^{-1} for 300 MW electric power.
d) Discharge of this wastewater is not allowed.

The legislation is called "Rahmen-Abwasser VwV[1] 1992 nach §7a WHG[2] (2002)" (Framework Regulation for Sewage), which was amended by the AbwV[3] (2004). This regulation prohibits the mixing or dilution of wastewater in order to meet the limiting values. In contrast to the Indirekteinleiterverordnung (Section 2.4.2.1), this regulation is valid for all states of the FRG. The rules which apply,

1) *V*er*w*altungs*v*orschrift, regulation.
2) *W*asser*h*aushalts*g*esetz, water resource policy law.
3) *Ab*wasser*v*erordnung, regulation for wastewater.

however, depend on the size of the municipalities (Appendix 1) and cover 56 industrial fields (Appendices 2–57). Here, we only want to present two examples: Appendix 1 (municipalities; Table 2.9) and Appendix 47 (washing water containing fuel gases from power plants; Table 2.10).

All the necessary details concerning the collecting of samples, their preparation and analysis are given in AbwV.

In contrast to municipal wastewater (Table 2.9), the effluents of fuel gas washing typically contain high concentrations of heavy metals. According to the regulation, these must now be separated from the washing water. Nutrients such as nitrogen and phosphorus as well as biodegradable substances (BOD_5) contained in municipal wastewater are not considered as important pollutants here.

2.4.3
EU Guidelines

In these guidelines, the qualities of four different surface waters are described according to their concentration, pH, temperature, color and 42 further parameters, which must not be exceeded (AbwV.; Schulz and Becker 2004). The following guidelines are valid for four different purposes:

- for surface water used for drinking water production,
- for surface water used for swimming and bathing (see Section 12.5),
- for fish farming,
- for mussel farming.

Two types of values are to be distinguished: (a) I-values (which are obligatory = *i*mperative) and (b) G-values (which are guide values = *g*uidelines).

Three types of surface water preparation must be distinguished for drinking water production:

A 1, simple physical methods.
A 2, normal physical and chemical methods.
A 3, advanced physical and chemical methods.

These guidelines for the limitation of *immissions* are characterized by the following advantages compared with such legislation, which is valid for the limitation of emissions (Rahmen-Abwasser VwV 1992):

- A better economical efficiency for all WWTPs; the degree of wastewater treatment is directly linked to the quality demands on the surface water generated, and unnecessary expenditures can be avoided.
- The quality of the treated wastewater can be controlled in such a way to ensure that the surface water can be used as planned.
- The total pollution of the surface water and its capacity of self-purification are considered.
- Different qualities of treated water can be defined in order to stabilize the ecological equilibrium.

The following disadvantages should be considered:

- No experience has been gained with the sampling frequency and the allowed differences of high-tide values from the guideline values.
- There may be problems if the discharged treated wastewater is to be controlled, because the receiving capacity depends greatly on the quality of the receiving water.

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