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Input-Dependent Life-Cycle Inventory Model of Industrial Wastewater-Treatment Processes in the Chemical Sector

ANNETTE KÖHLER,*,† STEFANIE HELLWEG,‡ ERCAN RECAN,§ AND KONRAD HUNGERBÜHLER§

Empa, Technology and Society Laboratory, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland, ETH Zurich, Institute of Environmental Engineering, CH-8093 Zürich, Switzerland, and ETH Zurich, Institute for Chemical and Bioengineering, CH-8093 Zürich, Switzerland

Industrial wastewater-treatment systems need to ensure a high level of protection for the environment as a whole. Life-cycle assessment (LCA) comprehensively evaluates the environmental impacts of complex treatment systems, taking into account impacts from auxiliaries and energy consumption as well as emissions. However, the application of LCA is limited by a scarcity of wastewater-specific life-cycle inventory (LCI) data. This study presents a modular gate-to-gate inventory model for industrial wastewater purification in the chemical and related sectors. It enables the calculation of inventory parameters as a function of the wastewater composition and the technologies applied. For this purpose, data on energy and auxiliaries' consumption, wastewater composition, and process parameters was collected from chemical industry. On this basis, causal relationships between wastewater input, emissions, and technical inputs were identified. These causal relationships were translated into a generic inventory model. Generic and site-specific data ranges for LCI parameters are provided for the following processes: mechanical−biological treatment, high-pressure wet-air oxidation, nanofiltration, and extraction. The input- and technology-dependent process inventories help to bridge data gaps where primary data are not available. Thus, they substantially help to perform an environmental assessment of industrial wastewater purification in the chemical and associated industries, which may be used, for instance, for technology choices.

Introduction

The environmental assessment of industrial wastewater-treatment systems is becoming increasingly important due to modern environmental regulations (*1*, *2*). These regulations require the reduction or prevention of emissions to air, water, and soil in order to achieve a high level of protection for the environment as a whole. Life-cycle assessment (LCA) is adequate for such an integrated assessment, as it takes into account the entire system of industrial wastewater treatment including upstream and downstream processes. LCA has previously been applied for specific wastewater-treatment techniques (*3*−*7*) and for highly contaminated wastewaters and sludge (*8*−*10*). These surveys present the aggregated overall results of comparative life-cycle assessment studies. The inventory data on a unit-process level is not given; nor are the procedures for assigning emissions and consumption of energy and auxiliaries to the wastewater input revealed. Therefore, industrial wastewater-specific life-cycle inventory (LCI) data cannot be calculated using these methods. Until now, a comprehensive model for a complex industrial wastewater-treatment system, consisting of various physicochemical and biological purification operations, that accounts for process- and wastewater-input dependent emissions and auxiliary use, has not been published.

The goal of this paper is to establish a modular gate-to-gate inventory model of industrial wastewater purification in the chemical sector for application in LCA. This model will facilitate the calculation of inventory data as a function of the wastewater composition and the technologies applied. The model considers current state-of-the-art, large-scale technologies operated in chemical industry at large industrial sites (*2*).

Methods

Description of Industrial Wastewater Treatment Processes under Study. The inventory model is based on two established end-of-pipe wastewater treatment systems (WWTS) operated by Ciba Specialty Chemicals in Grenzach, Germany. At this industrial site, about 100 different high-quality specialty chemicals along with some corresponding basic chemicals are manufactured in multi-batch operations. Up to 1000 different complex process wastewaters with an annual volume of more than 500 000 m^3 and external chemical and pharmaceutical wastewaters are purified. The first WWTS, operated until 2003, comprises a combination of nanofiltration, extraction, high-pressure wet-air oxidation, and activated sludge treatment units (Figure 1). The sludge generated in the mechanical−biological treatment plant (MBTP) was incinerated on-site. The single process-wastewater streams originating from the various production facilities were collected as cumulative wastewater flows (WW 1 to 4) according to criteria such as biodegradability and total organic carbon (TOC) load, feeding the different treatment installations (Figure 1).

In the second WWTS (system 2), established in 2003, the highly concentrated wastewaters from both the nanofiltration and the extraction unit are combusted together with the MBTP sludge in the incineration plant (Figure 1). Thus, the non- and hardly biodegradable organic wastewater pollutants are mineralized by incineration, while in system 1 the wet-air oxidation process (WAOP) was employed for their elimination.

The wastewater treatment technologies studied are shown in Figure 2. Process characteristics, operating parameters, and treatment requirements for *individual* wastewaters are described in the Supporting Information. For processes' application spectra and requirements for the *tributary wastewater mixes* see Figure 1.

Scope of the Model: Functional Unit and System Boundaries. The gate-to-gate inventory tool can be used, first, to assess the treatment of chemical wastewaters with various compositions and, second, to compare alternative technology options. The model has a modular structure, so

* Corresponding author phone: +41-44-633 49 92; fax: +41-44-633 10 61; e-mail: annette.koehler@ifu.baug.ethz.ch.
† Empa, Technology and Society Laboratory.
‡ ETH Zurich, Institute of Environmental Engineering.
§ ETH Zurich, Institute for Chemical and Bioengineering.

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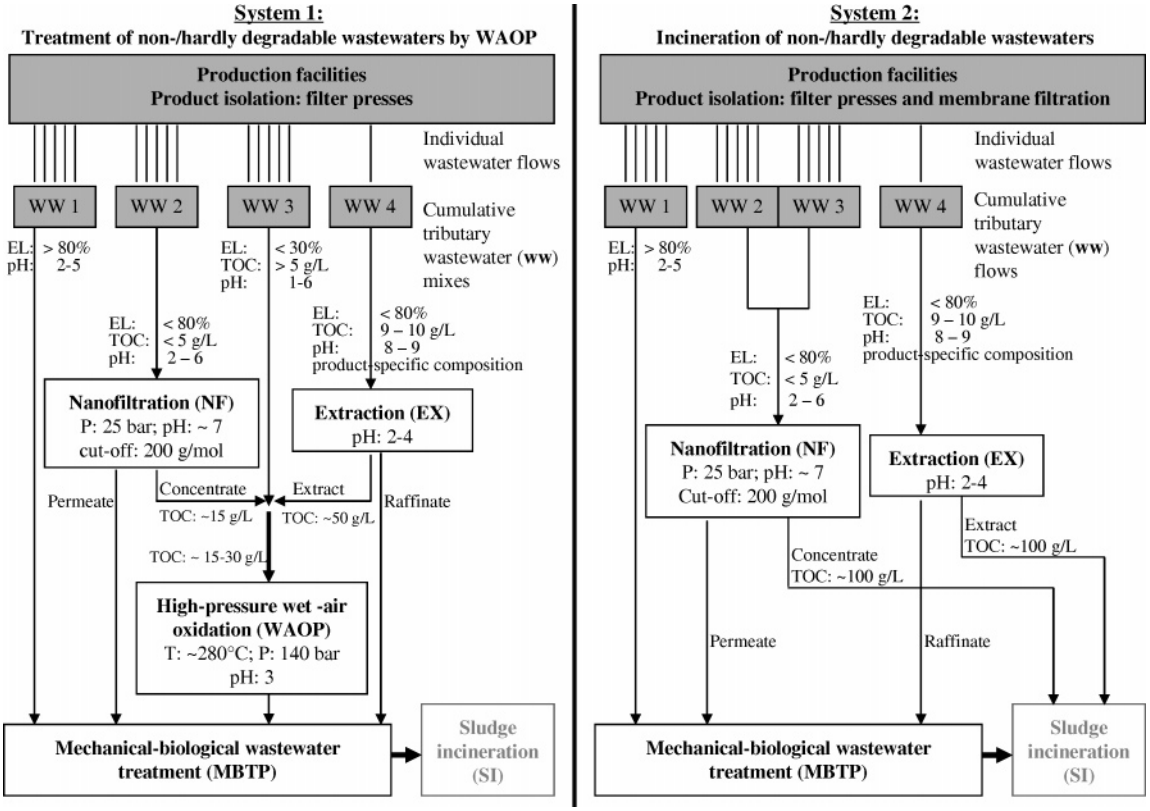

FIGURE 1. Wastewater treatment systems under study. TOC: total organic carbon, EL: TOC elimination by biological treatment in Zahn-Wellens test.

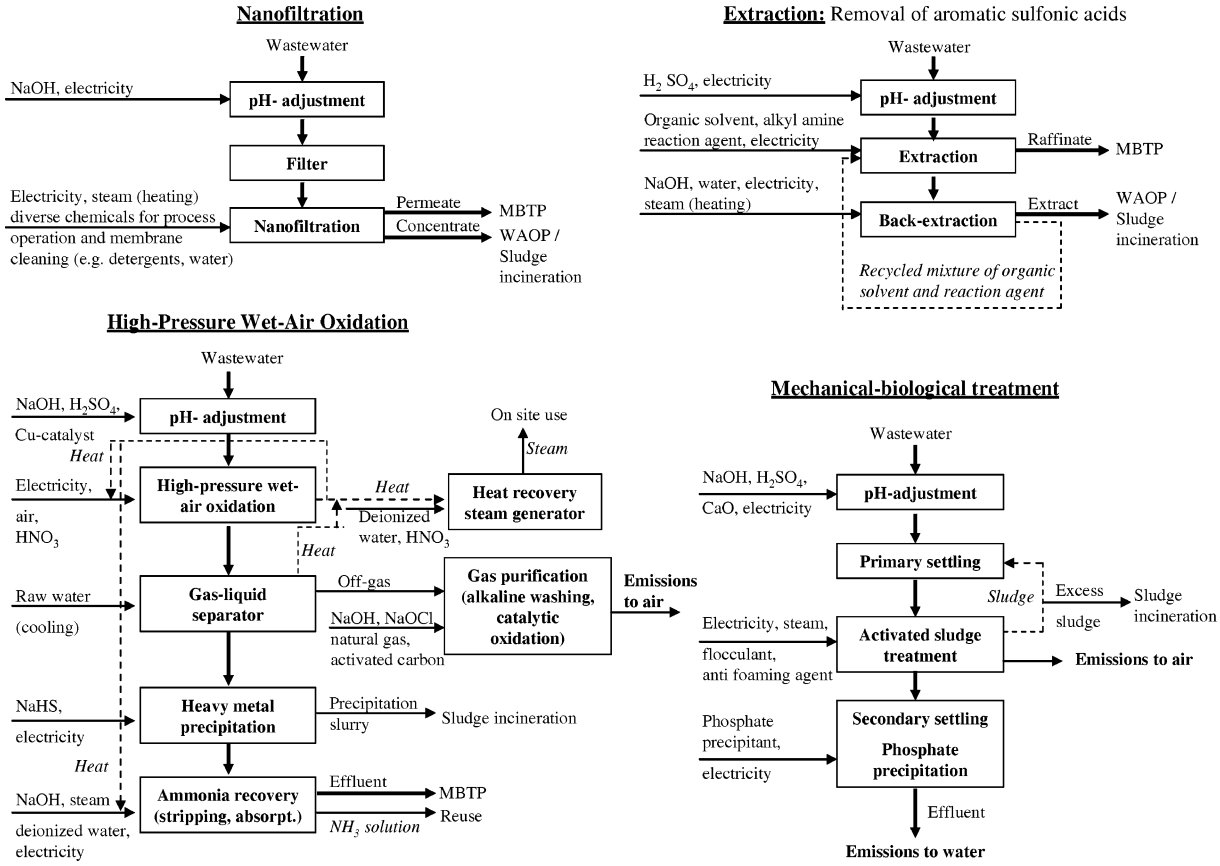

FIGURE 2. Flow charts of the wastewater-treatment technologies.

that diverse treatment units can be combined, depending on the characteristics of the wastewater to be treated. For the calculation of *wastewater-specific* inventories, the wastewater input needs to be specified on the level of specific organic and inorganic wastewater parameters. The functional unit of the inventory model was defined as follows.

Treatment of a certain volume of wastewater from chemical industry or allied industrial branches with a composition being characterized by the following 14 parameters: total organic carbon (TOC_{total}, $TOC_{degradable}$, $TOC_{refractory}$); adsorbable organically bound halogens (AOX); nitrogen compounds (N_{total}, NH_4^+-N, NO_3^--N, NO_2^--N); phosphorus compounds (PO_4^{3-}-P); heavy metals (Cu_{total}, Cr_{total}); and inorganic anions (Cl^-, Br^-, SO_4^{2-}).

This basic parameter set includes main parameters reflecting performance rates and process efficiencies (e.g., TOC, N_{total}) (*2, 11*) and key wastewater pollutants regulated by European policies (*1, 2, 11, 12*). Parameter values were obtained for all inflows and outflows of the modeled purification processes. Organic pollutants are quantified in terms of sum parameters, such as TOC, because individual organic compounds are generally not measured throughout the entire treatment system. Also, some heavy metals, such as Zn and Pb, were not taken into consideration because of missing data.

The wastewater volume referring to the inventory model presented here is 1 m^3. Since the wastewater composition may vary considerably between different industrial wastewater-producing activities, the functional unit has to be specified in regard to the pollutant concentrations within the context of each LCA study.

The gate-to-gate system boundaries encompass the processes extraction, nanofiltration, high-pressure wet-air oxidation with gas purification, and mechanical−biological purification, as well as the site-internal wastewater collection. The sludge dewatering and incineration was not considered because models are available from the literature (*13, 14*). Regarding the life-cycle stages of the treatment installations, only the operation of the plants is considered in the model, while capital goods were excluded. The inventories comprise the quantities of several energy carriers and various auxiliary chemicals applied in the wastewater treatment processes. However, the upstream processes for external generation of electricity and steam, for production of auxiliaries, and downstream processes of waste disposal are left outside the gate-to-gate system boundaries. Similarly, the transports of auxiliaries were not taken into account. Such background inventory data can easily be retrieved from LCI databases (e.g., the ecoinvent database (*15*)).

Inventory Model Design and Allocation. The system *industrial wastewater treatment* reflects a multi-input/multi-output scheme, with diverse wastewater streams of various compositions entering the system and diverse outputs produced by the system. Among the latter are the produced steam and recovered ammonia solution for reuse (Figure 2). Therefore, allocation, which describes the partitioning of the input and output flows of a unit process to the different products or functions under study, is conducted. For the present systems model, allocation mainly focused on physicochemical causalities. The consumption of energy carriers and auxiliaries, the associated emission of pollutants, as well as the production of coproducts, were allocated to the wastewater input according to the specific causal relationships.

Process-dependent consumption and emissions do not depend on the properties and composition of the wastewater input, but merely on the wastewater input as a whole and on the process conditions. For process-dependent emissions, no distinct relation to the wastewater input can be established. Such process-dependent emissions and auxiliary materials' consumption were assumed to be proportional to the operating period of the respective treatment plant. Therefore, the resulting process-specific burdens were allocated to 1 m^3 of wastewater treated as a total.

In contrast, product-dependent inputs and outputs are a function of the wastewater properties, i.e., the wastewater composition. The underlying physical and chemical relationships were examined in order to connect the auxiliaries' consumption, energy inputs, and pollutant releases to the originary wastewater components. Product-dependent allocation was performed either to the mass of the originary wastewater elements or by stoichiometrical assignment to the related wastewater components. Likewise, the coproducts generated in the wastewater treatment system, such as ammonia solution in the WAOP, were allocated to the wastewater components from which they stem.

Relationships between auxiliaries' and energy inputs and wastewater properties are presented by *consumption factors*. Consumption factors define the mass, volume, or energy content of auxiliaries or energy carriers used per 1 m^3 of wastewater or per mass unit of the wastewater element, respectively. For the calculation of process-dependent and product-dependent consumption factors see eqs 1and 2.

$$cf_{A,process} = \frac{consumption_A}{v_{WW}} \text{ [consumption unit/m}^3\text{]} \quad (1)$$

where $cf_{A,process}$ is the process-dependent consumption factor for auxiliary material or energy carrier A (given in kg/m^3, $m^3{}_n/m^3$, or MJ/m^3), $consumption_A$ is the consumed mass, volume, or energy quantity of auxiliary material or energy carrier A (in kg, $m^3{}_n$, or MJ), and v_{WW} is the process-related wastewater input volume (in m^3).

$$cf_{A,product,i} = \frac{consumption_A}{mass_i} \text{ [consumption unit/kg]} \quad (2)$$

where $cf_{A,product,i}$ is the product-dependent consumption factor for auxiliary material or energy carrier A (given in kg/kg, $m^3{}_n$/kg, or MJ/kg), $consumption_A$ is the consumed mass, volume, or energy quantity of auxiliary material or energy carrier A (in kg, $m^3{}_n$, or MJ), and $mass_i$ is the mass of wastewater element i (in kg), which triggers the auxiliaries or energy consumption.

Coproducts, e.g., steam, are internally produced by the WAOP. This internal coproduct generation is also represented by consumption factors with a negative value. When implementing the modular wastewater-system model in a comparative LCA study, it must be considered whether the coproducts have a positive economic value and can thereby substitute a product manufactured by other technical systems. System expansion can be applied to include the additional functions related to the coproducts (*16*).

In the model presented here, the relation between the inflow wastewater and the outflow wastewater, sludge, or the emissions to air and receiving water body are described by *transfer coefficients*. Transfer coefficients express the partitioning of substances and elements between different output streams of the system. They were determined on the basis of an average wastewater feed into each treatment process and calculated by means of a flow analysis of the wastewater components (eq 3).

$$tc_{i,j} = \frac{z_{i,j}}{m_{i,j}} \times 100 \text{ [\%]} \quad (3)$$

where $tc_{i,j}$ is the transfer coefficient for wastewater element i ($i = 1, 2, ..., n$) conveyed to output j ($j = 1, 2, ..., m$), $z_{i,j}$ is the mass of wastewater element i in the process output stream j (e.g., in the effluent) (in kg), and $m_{i,i}$ is the mass of element i in the average wastewater input (in kg).

Given the average input mass, the element mass transferred to each output stream of every treatment pro-

TABLE 1. Consumption Factors (*cf*) for the Treatment Processes Extraction, Nanofiltration, High-Pressure Wet-Air Oxidation, and Mechanical−Biological Treatment

energy/auxiliaries consumption	unit	average (±SD) ($n = 42$)[a] extraction	nanofiltration	high-pressure wet-air oxidation	mechanical−biological treatment
process-dependent allocation on wastewater volume					
steam[b]	kg/m³	10.2 (±4.67)	8.20 (±3.28)		0.12 (±0.07)
electricity	MJ/m³	90.5 (±18.0)	79.6 (±7.17)/ 87.6 (±17.0)[c]	334 (±28.8)[m]	
nitrogen gas	dm^3_n/m^3	6.64 (±4.39)			
deionized water	L/m³		73.2 (±7.91)		
H_2SO_4 (96%)	kg/m³	8.03 (±0.74)		13.17 (±6.30)[m]	0.22 (±0.06)[m]
HCl (50%)	kg/m³		0.02 (±0.01)		
HNO_3 (50%)	kg/m³			1.85 (±0.29)	
NaOH (50%)	kg/m³		0.60 (±0.15)	36.*5* (±4.44)[m]	0.56 (±0.23)[m]
NaOCl (14%)	kg/m³			0.37 (±0.09)	
NaHS (30%)	kg/m³			0.11 (±0.04)	
CaO	kg/m³				0.49 (±0.10)
flocculant	g/m³				4.27 (±2.38)
anti-foaming agent	g/m³		5.55 (±3.08)		13.7 (±2.47)
cleaning agent	g/m³		29.7 (±12.5)		
detergents	g/m³		23.6 (±10.1)		
engine lubricating oil	g/m³			79.5 (±4.99)	
product-dependent allocation on wastewater element mass					
steam[b]	kg/kg N_{total}			1.13 (±0.30)	
electricity	MJ/kg NH_4^+−N				10.2 (±2.55)[d,e]
electricity	MJ/kg $TOC_{degradable}$				7.70 (±1.92)[f,e]
electricity	MJ/kg NO_3^-−N				−5.51(±1.38)[g,f]
natural gas	dm^3_n/kg TOC_{total}			30.8 (±4.88)	
deionized water	L/kg TOC_{total}			16.2 (±0.99)[h]	
deionized water	L/kg $TOC_{refractory}$	11.2 (±0.52)/ 9.45 (±3.15)[c]			
deionized water	L/kg N_{total}			11.9 (±1.25)[h]	
raw water (origin: river water)	L/kg TOC_{total}			678 (±87.3)	
NaOH (50%)	kg/kg $TOC_{refractory}$	1.51 (±0.26)			
organic solvent	g/kg $TOC_{refractory}$	15.1 (±0.69)			
alkyl-amine reaction agent	g/kg $TOC_{refractory}$	2.49 (±1.18)			
$CuSO_4$ (catalyst)	g/kg TOC_{total}			2.40 (±0.13)[i]	
phosphate precipitant ($Na_2Al_2O_4$)	kg/kg PO_4^{3-}−P				5.29 (±1.32)[j,e]
activated carbon	g/kg TOC_{total}			3.93 (±1.09)	
coproducts					
steam[b]	kg/kg TOC_{total}			− 2.59 (±0.48)[k]	
NH_3 (25%)	kg/kg N_{total}			− 1.16 (±0.12)[l]	

[a] Number *n* of values in the sample determined monthly during the years 2000−2004 (see Supporting Information, Table S-2). [b] Energy content: 2810 kJ/kg. [c] Top value for system 1 ($n = 36$), bottom value for system 2 ($n = 6$). [d] Ref *17*. [e] 25% SD assumed. [f] Converted from the energy consumption factor for BOD (0.801×10^{-3} kWh/g BOD) reported by ref *17* with a ratio for $BOD/TOC_{degradable}$ of 2.67. [g] Denitrification of NO_3^- to N_2 releases elementary oxygen and thus reduces the electricity consumption needed for aeration. [h] The consumption of deionized water is split between the steam generation in the heat-recovery unit (90%) and the ammonia stripping (10%). [i] Copper catalyst is added if Cu concentration in WAOP inflow is below 10 g/m³. [j] The consumption factor was calculated stoichiometrically (excess factor: 2) (see Supporting Information). [k] The steam mass generated represents the net steam production from the oxidation sub-process (steam demand for ammonia stripping considered separately). [l] Ammonia recovery. [m] Based on expert judgment.

cess can be summarized in a technology-specific matrix equation (eq 4).

$$\begin{pmatrix} m_{11} & 0 & \dots & 0 \\ 0 & m_{22} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & m_{nn} \end{pmatrix} \cdot \begin{pmatrix} tc_{11} & tc_{12} & \dots & tc_{1m} \\ tc_{21} & tc_{22} & \dots & tc_{2m} \\ \dots & \dots & \dots & \dots \\ tc_{n1} & tc_{n2} & \dots & tc_{nm} \end{pmatrix} = \begin{pmatrix} z_{11} & z_{12} & \dots & z_{1m} \\ z_{21} & z_{22} & \dots & z_{2m} \\ \dots & \dots & \dots & \dots \\ z_{n1} & z_{n2} & \dots & z_{nm} \end{pmatrix} \quad (4)$$

where *n* is the number of wastewater components specified in the functional unit, and *m* is the number outputs for the technology selected.

By applying the transfer-coefficient approach, the wastewater-element flows and the associated product-specific emissions can be calculated as a function of the wastewater composition throughout the entire wastewater treatment system, as each of the technologies is represented by a set of transfer coefficients. Transfer coefficients and consumption factors for all treatment processes were calculated as average values supplemented by the standard deviation (SD). For data sources see the Supporting Information.

Results

For all treatment processes consumption factors and transfer coefficients for the relevant wastewater components were calculated applying the allocation principles described above (see Methods). Each unit-process module can be used for the calculation of inventories for wastewater-treatment arrays composed of different wastewater-purification technologies. Consumption factors and transfer coefficients are given in Tables 1 and 2, respectively. Allocation procedures are described in more detail in the Supporting Information.

TABLE 2. Transfer Coefficient (*tc*) for the 14 Wastewater Parameters in the Treatment Processes Extraction, Nanofiltration, High-Pressure Wet-Air Oxidation (WAOP), and Mechanical−Biological Treatment (MBTP)

	average (±SD) (in %)												
	extraction (system 1 & 2) ($n = 42$)[a]		nanofiltration (system 1) ($n = 36$)[a]		nanofiltration (system 2) ($n = 6$)[a]		high-pressure wet-air oxidation (system 1) ($n = 36$)[a]				mechanical−biological treatment (system 1 & 2) ($n = 42$)[a]		
pollutants in the wastewater input	extract to WAOP/SI[b]	raffinate to MBTP	concentrate to WAOP	permeate to MBTP	concentrate to SI	permeate to MBTP	effluent to MBTP	precipitation slurry to SI[b]	recovery as NH_3 solution	emission to air	emission to water	emission to air	sludge to SI
TOC_{total}	89.5 (±1.6)	10.5 (±1.6)	55.9 (±4.7)	44.1 (±4.7)	73.1 (±6.8)	26.9 (±6.8)	7.7 (±1.9)	0.1[c] (±0.1)		92.2[d] (±1.9)	22.8 (±5.9)	23.0[e] (±5.9)	54.2 (±5.9)
$TOC_{degradable}$	61.9 (±13.3)	38.1 (±13.3)	23.7 (±9.1)	76.3 (±9.1)	41.2 (±14.1)	58.8 (±14.1)	25.2 (±9.8)	0.1[c] (± 0.1)		74.7 (±9.8)		28.6[e] (±5.6)	71.4 (±5.6)
$TOC_{refractory}$	96.5 (±1.3)	3.5 (±1.3)	73.0 (±5.7)	27.0 (±5.7)	80.2 (±5.2)	19.8 (±5.2)	2.0 (±1.0)	0.1[c] (±0.1)		97.9 (±1.0)	100.0[f] (±1.0)		
AOX	91.8 (±5.4)	8.2 (±5.4)	45.1 (±22.3)	54.9 (±22.3)	66.3 (±15.1)	33.7 (±15.1)	14.4 (±6.1)	0.1[c] (±0.1)		85.5[g] (±6.1)	36.5 (±20.7)		63.5 (±20.7)
N_{total}	65.2 (±6.1)	34.8 (±6.1)	12.4 (±10.1)	87.6 (±10.1)	29.6 (±7.4)	70.4 (±7.4)	30.4 (±13.2)	0.1[c] (±0.1)	23.9[h] (±1.2%)	45.6[i] (±13.2)	44.0 (±11.9)	32.9 (±11.9)	23.1 (±11.9)
NH_4^+−N	61.5 (±4.5)	38.5 (±4.5)	14.1 (±10.8)	85.9 (±10.8)	15.3 (±12.2)	84.7 (±12.2)	28.5 (±17.3)	0.1[c] (±0.1)	26.6[h] (±1.4)	44.8 (±17.3)	51.6[j] (±18.8)	28.9[k] (±18.8)	19.5 (±18.8)
NO_3^-−N	28.2 (±25.5)	71.8 (±25.5)	11.2 (±4.6)	88.8 (±4.6)	14.0 (±7.5)	86.0 (±7.5)	68.4 (±16.1)	0.1[c] (±0.1)		31.5[l] (±16.1)	26.7 (±17.5)	70.1[m,n] (±17.5)	3.2 (±17.5)
NO_2^-−N	90.2 (±2.3)	9.8 (±2.3)	10.0 (±3.0)	90.0 (±3.0)	11.8 (±7.5)	88.2 (±7.5)	99.9[o] (±1.0)	0.1[c] (±0.1)			59.9[p,n] (±15.0)	38.4 (±15.0)	1.7 (±15.0)
PO_4^{3-}−P	6.6 (±17.5)	93.4 (±17.5)	47.5 (±3.2)	52.5 (±3.2)	49.6 (±3.5)	50.4 (±3.5)	99.9[q] (±1.0)	0.1[c] (±0.1)			8.2 (±7.9)		91.8 (±7.9)
Cu_{total}	50.4 (±35.4)	49.6 (±35.4)	60.1 (±25.7)	39.9 (±25.7)	68.3 (±21.7)	31.7 (±21.7)	35.2[r,s] (±26.9)	64.8[r] (±26.9)			21.9 (±14.3)		78.1[t] (±14.3)
Cr_{total}	16.1 (±25.0)	83.9 (±25.0)	52.8 (±28.7)	41.3 (±28.7)	71.3 (±12.5)	28.7 (±12.5)	45.6[r] (±18.1)	54.4[r] (±18.1)			33.2[u] (±15.1)		66 8[t] (±15.1)
Br^-	22.4 (±27.3)	77.6 (±27.3)	8.1 (±6.2)	91.9 (±6.2)	34.1 (±6.4)	65.9 (±6.4)	97.8 (±21.9)	2.1[v] (±21.9)		0.1[v] (±0.1)	99.5 (±15.0)		0.5 (±15.0)
Cl^-	3.7 (±6.6)	96.3 (±6.6)	6.4 (±5.7)	93.6 (±5.7)	21.3 (±10.4)	78.7 (±10.4)	95.6 (±9.4)	4.3[v] (±9.4)		0.1[v] (±0.1)	98.6 (±7.9)		1.4 (±7.9)
SO_4^{2-}	1.0 (±1.0)	99.0[w] (±1.0)	24.5 (±12.7)	75.5 (±12.7)	40.4 (±8.0)	59.6 (±8.0)	99.5[w] (±1.0)	0.5 (±1.0)			99.5 (±3.8)		0.5 (±3.8)

[a] Number *n* of measurements used in the calculations (sampling period: 2000−2004; see Supporting Information, Table S-2). [b] SI: Sludge incineration. [c] Due to lack of data, an average transfer coefficient of 0.1% (up to maximum 0.2%) for the wastewater constituents transferred into the waste slurry was assumed. [d] Emitted as CO_2. [e] Emitted as CO_2. For quantification of the CO_2 mass emitted see calculations in Supporting Informatio [f] $TOC_{refractory}$ comprises the non-biodegradable and non-adsorbable TOC. [g] AOX emitted as CO_2 and halogens after waste-gas oxidation. [h] Transfer of nitrogen to ammonia solution by stripping. [i] Nitrogen is emitted to air as N_2. [j] 40.6% emitted as NH_4^+-N, 11.0% nitrified to and emitted as NO_3^--N (chemical transformation considered). [k] Emission to air as N_2 after nitrification and denitrification. [l] NO_3^--N reduced to N_2. [m] Denitrification of NO_3^--N to N_2 in denitrification zone of activated sludge bed. [n] SD assumed to be 25% of the average value. [o] Additional NO_2^--N is created by the decomposition of organic compounds carrying NO_2-substituents. This additional NO_2^--N mass is not included in the transfer coefficient. [p] 45.3% emitted as NO_2^--N; 14.6% nitrified to and emitted as NO_3^--N. [q] Additional phosphate is created from the oxidation of organic substances containing phosphorus. This share of phosphate created is not included in the transfer coefficient. [r] Transfer of heavy metals (Cu, Cd) to air was neglected. [s] The WAOP effluent contains additional copper from the catalyst applied. This copper mass has to be additionally calculated taking into account the transfer into the precipitation slurry (see transfer coefficient in this table). [t] Heavy metals are eliminated from the wastewater by adsorption to activated sludge. [u] 16.3% of this fraction is released to the receiving water body as dissolved hexavalent chromium. [v] No information on the exact composition of the waste gas and the waste slurry was available. Fractions of halogens transferred to air were assumed to be 0.1% and the transfer to the waste slurry was calculated from the remainder. [w] The raffinate and the WAOP effluent contain additional sulfate stemming from the pH-adjustment with sulfuric acid. This sulfate mass has to be calculated separately according to the consumption of H_2SO_4 in the respective process (see consumption factors in Table 1).

Extraction Process. Apart from the energy carriers and acid solution, all auxiliary chemicals used in the extraction process are needed for the removal of recalcitrant organic pollutants. Therefore, their consumption was assigned to $TOC_{refractory}$. Since the organic solvent and the alkyl amine reactant are recovered in the back-extraction sub-process by ~25% and ~65%, respectively, the consumption factors for these chemicals merely account for additional amounts compensating chemical loss (Table 1).

Transfer coefficients of the extraction process are alike for both WWTS (Table 2). The higher TOC concentration in the extract necessary to feed the sludge incineration (Figure 1, system 2) is achieved by applying a higher concentrated base and thus less deionized water for the back-extraction process (see $cf_{deionizedwater,product,TOCrefractory}$ in Table 1).

Nanofiltration Process. The nanofiltration filtration represents a pure physical separation process of all wastewater contaminants. As no clear relationship to any specific wastewater element can be established, all energy carriers and auxiliary products are assigned to the wastewater volume treated (Table 1). In order to obtain higher organic carbon concentrations in the nanofiltration concentrate for subsequent incineration (system 2), the removal of organic pollutants is increased by redirecting a 10% fraction of the concentrate into the feed stream of the nanofiltration subunits. Therefore, electricity demand was assumed to increase by 10%, which is caused by a slightly higher transmembrane pressure (see $cf_{electricity,process}$ in Table 1). The use of sodium hydroxide cannot be allocated to the wastewater pH due to the strongly varying pH value of the mixed wastewater input (WW2). Auxiliaries such as detergents, the cleaning agent, and hydrogen chloride solution are occasionally employed for membrane washing and therefore represent a process-dependent consumption (Table 1).

For organic contaminants as well as dissolved inorganic ions, transfer coefficients are significantly higher in system 2, comprising the combustion of the concentrates, than in system 1, including the WAOP (Table 2). This is due to the enhanced concentration efficiency by stream redirection.

High-Pressure Wet-Air Oxidation Process. The consumption of most auxiliaries and electricity applied in the high-pressure wet-air oxidation process was modeled process-dependently since it was caused by the treatment of the entire wastewater. Some auxiliary materials, however, are determined by specific wastewater elements because of the chemical reactions involved. For instance, the consumption of auxiliaries employed for the off-gas purification (e.g., activated carbon and natural gas) is assigned to the TOC_{total} mass input, which is oxidized in the WAOP. Similarly, allocation of auxiliary products to the N_{total} input mass (e.g., steam) is performed for auxiliaries used for ammonia stripping (Table 1).

Coproducts generated are allocated to the wastewater elements from which they originate. Steam is produced due to heat release in the oxidation process of the organic contaminants present (expressed as TOC_{total}) and ammonia solution is generated from the nitrogen-containing wastewater constituents (Table 1).

Overall, the wet-air oxidation achieves extremely high performance rates for the removal of organic contaminants by oxidation to CO_2. This is reflected by high transfer coefficients to air ($t_{TOC_{total},air}$ > 90%) (Table 2). Transfer coefficients for nitrogen-containing contaminants are more diverse. In addition to being recovered to a large extent ($t_{NH_4-N,ammonia}$=26.6%) as ammonia solution, ammonium is oxidized to nitrogen and emitted to air. In contrast, nitrate functions as additional oxidant in the WAOP. Thus a significant share ($t_{NO_3-N,air}$ = 31.5%) is reduced to elementary nitrogen and released to air. The precipitation subprocess effectively eliminates heavy metals with transfers of greater than 50% to the waste slurry.

Mechanical−Biological Treatment Process. Because the temporally variable pH conditions impede a stoichiometrical allocation, all auxiliary chemicals (NaOH, H_2SO_4, CaO) applied for neutralization of the MBTP inflow wastewater are allocated to the wastewater volume. Product-related allocation was performed for auxiliary chemicals employed for flocculation and precipitation. The mechanical−biological wastewater treatment is operated in order to microbiologically decompose organic substances and remove nitrogen compounds. Therefore, all electricity demands were allocated to the causing wastewater constituents $TOC_{degradable}$ and the nitrogen species (Table 1; for additional explanations and calculation see Supporting Information).

In the MBTP, nitrogen is present in various chemical species which are converted into each other by microbial degradation processes. The transfer coefficients for nitrogen species consider the overall transfer from the inflow wastewater to sludge and air (Table 2). For additional information on the substance flows of nitrogen species see the Supporting Information (Table S-3). CO_2 emissions to air are specified according to the organic pollutants in the wastewater input which stem from the application of organic chemicals in synthesis. As organic chemicals are mainly produced from fossil fuels, the carbon source is of fossil origin (for quantification of CO_2 emissions see the Supporting Information). Heavy metals are merely eliminated by adsorption into the biological sludge, while salt anions are almost entirely released to the receiving water body (Table 2).

Discussion

Model Applicability. Within the context of LCA, only a few studies have investigated different treatment technologies for industrial wastewater, some of them as technology arrays representing a specific treatment arrangement (*3*−*7*), others as techniques supplementing existing wastewater treatment systems (*8*−*10*). Primarily, these LCA studies presented cumulative LCA results, while disaggregated inventory data is hardly available. To the authors' knowledge, the model setup created within the current work is the first to provide, for the chemical sector, an input-dependent modular model of an integrated wastewater treatment system to this degree of complexity. It enables the calculation of wastewater-specific inventory data for state-of-the-art large-scale purification technologies employed for the end-of-pipe treatment of chemical wastewaters containing a wide range of organic pollutants. Moreover, it covers wastewaters from multi-production-mix enterprises as well as from small companies producing only a few products. The inventory model as a whole as well as the individual unit-process inventories are applicable to wastewaters from the production of basic, specialty, and fine chemicals and pharmaceutical products, as long as the overall treatment requirements specified are met (*2, 11*). Since the unit-process modules for the physicochemical and mechanical−biological treatment techniques separately display all input and output flows, they can also be combined with inventories of other unit operations (e.g., evaporation, flotation) according to technical feasibility, regulatory standards, and discharge limitations for the case to be investigated. The application of the process inventories is, however, restricted to treatment facilities with similar wastewater-input characteristics (see Supporting Information), operating conditions, and process equipment (Figure 2). For instance, the treatment conditions (temperature, pressure) for the WAOP of pulp and paper and petrochemical effluents are similar (*18*) to those of the plant investigated. Therefore, the WAOP inventory of the present study may also be used to estimate the energy and auxiliaries' con-

sumption for WAOP treatment of pulp and paper and petrochemical effluents.

Representativeness of Process Modules. In the present study, the consumption factors and transfer coefficients for the industrial wastewater-treatment modules were primarily obtained from the analysis of industry data. They are based on broad empirical data with an exceptionally comprehensive set of measurements data for the wastewater parameters and auxiliaries. This allowed for the determination of the average value and the standard deviation for all inventory parameters.

For the mechanical−biological wastewater treatment, the basic allocation principles and procedures chosen in this study are similar to other inventory models for municipal wastewater treatment. Transfer coefficients for organic wastewater components and metals are comparable to the value ranges of transfer coefficients reported for municipal wastewater purification (e.g., for TOC_{total} and copper) (*2, 13, 17*) and to other empirical data (*19, 20*). By contrast, phosphate and nitrogen are more efficiently eliminated ($tc_{PO_4-P,sludge} = 91.8\%$, $tc_{N_{total},air} = 32.9\%$) than in municipal plants (e.g., 48.2% for PO_4^{3-}-P removal and 5.2% for nitrogen removal to air according to refs *13* and *17*). This is due to the state-of-the-art technologies applied for nitrification, denitrification, and phosphate removal as legally required for large industrial sites (*2, 21*). The general accordance with our study confirms the generic validity of the MBTP model.

The transfer coefficients provided for the high-pressure wet-air oxidation and the nanofiltration processes represent state-of-the-art performance rates for contaminant elimination (*2, 21*). The use of specific auxiliary chemicals for the nanofiltration and WAOP (e.g., H_2SO_4, NaOH, $CuSO_4$) is influenced by the feed-wastewater composition, particularly by the pH value and the copper concentration. The consumption for sulfuric acid and sodium hydroxide strongly relates to the pH ranges specified for the cumulative inflows. While primarily dependent on the flow rate, the electricity consumption of the nanofiltration is also influenced by the concentration efficiencies required for the subsequent WAOP and incineration and is thus mainly valid for the TOC concentration ranges given in Figure 1. Therefore, the inventory models for the nanofiltration and the wet-air oxidation have a semi-generic character. By contrast, the inventory data for the extraction process are site-specific due to the optimized process design for removal of sulfonic acids.

The proposed (semi-)generic inventory data are particularly valuable when data from life-cycle inventory databases are not available or primary data from industry are kept confidential. Moreover, the inventory parameters are helpful for industry itself because they can be employed as an approximation if no information on large-scale wastewater-treatment technologies is obtainable, for instance in wastewater-treatment planning phases or when wastewater treatment is outsourced to external companies.

Model Assumptions and Uncertainty. Various simplifying assumptions which affect the results of an LCA study were made for setting up the multi-input/multi-output system model. In particular, the classification of energy and auxiliary material consumption into process-dependent and wastewater-related inventory flows represents a simplification of the real process operations. In many cases, inventory flows depend on process conditions as well as on the wastewater composition. For example, the electricity consumption for operating the nanofiltration unit is also controlled by the wastewater composition, in addition to the wastewater volume, because some wastewater constituents (e.g., salts) influence the trans-membrane pressure. Thus, the choice of the allocation parameter imposes some uncertainty on the model.

Further uncertainty is introduced into the systems model by assuming the relationship between wastewater input and the auxiliary and energy consumption, as well as emissions and wet residues, to be linear. Linearity may be an oversimplified procedure of technology modeling for some specific cases and specific processes. First, the occurrence and amount of a wastewater element in the input wastewater influences the fate throughout the wastewater system. Second, several wastewater input components manipulate the transfer of other elements to the output streams (e.g., in the WAOP the decomposition of $TOC_{refractory}$ and thus its transfer into the WAOP effluent are strongly dependent on the amount of catalyst applied (*22*)). Third, specific processes such as nanofiltration are principally nonlinear. However, for the inventory model of the cross-flow nanofiltration we assumed a reversible formation of the covering layer and thus a steady-state permeate flow with constant mass transfer of wastewater components. Finally, the linearity assumption is only reasonable if emissions do not surpass the regulatory emission levels (see Supporting Information for emission standards of the chemical industry in, e.g., Germany). Otherwise, operation of the abatement techniques is adapted to reach legal compliance. When applying the process inventories, it is left to the user to verify that overall contaminants' emissions to the environment do not exceed the mandatory emission levels. In spite of the shortcomings, linear modeling is a common approach in LCA. In general, process models are developed for an average operating status (*13, 17, 23, 24*) without considering time-dependencies and substance-specific wastewater compositions.

The underlying data of the inventory parameters vary in quality. Transfer coefficients are based on direct measurements and, thus, are rather accurate. Consumption factors were, in many cases, calculated from the amounts of auxiliary materials and chemicals purchased for a certain treatment process. In a few instances, e.g., energy consumption for specific technical devices of the WAOP, estimation from industry experts was the basis for calculation of the consumption factors.

The inventory parameters TOC and AOX comprise extremely heterogeneous organic wastewater constituents. While this heterogeneous composition is not a problem for the assessment of eutrophication, which can be based on the parameter $TOC_{degradable}$, it represents a challenge for the assessment of toxicity. Representative transfer coefficients for individual organic compounds cannot be provided because only in exceptional cases, some selected toxic (priority) pollutants are traced throughout the treatment systems. They should then be included in the functional unit if appropriate data exist to properly model the emissions to nature from all treatment alternatives under comparison. Moreover, these individual pollutants usually only account for a small fraction of overall TOC mass and toxicity, while the major part of the organic pollutant load remains unknown (see, e.g., ref *25*). This unknown composition of TOC and AOX complicates the assessment of toxicity. For instance, the WAOP transforms organic contaminants into new, lighter species, with sometimes higher toxicity than the parent substances. One possible solution is to work with industrial-branch specific TOC ecotoxicity characterization factors, based on the whole-effluent toxicity approach, as recommended by ref *26*.

Overall, this paper presented a representative gate-to-gate systems model for the treatment of wastewaters primarily from chemical and pharmaceutical industry. The choice of technological options, the system boundaries, and the level of model sophistication will then depend on the goal and scope of the individual LCA study. The computation of wastewater-specific inventories for alternative treatment options should greatly contribute to decision-making pro-

cesses for technology choices in industry as well as for regulative authorities. Specifically, the flexible inventory model allows for in-depth analysis of environmental benefits and burdens associated with the operation of end-of-pipe purification technologies. Yet, it may also assist in the system's retrofit by implementing process-integrated measures and thereby provide incentive to shift efforts to contaminant reduction at source. Providing a broad basis of environmentally relevant data, the model may significantly improve the practicability of environmental assessment in the field of industrial wastewater treatment and enhance the application of life-cycle assessment in practice.

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Supporting Information Available

Detailed descriptions of the wastewater-treatment processes, information on industry-data sources, and additional information on the calculation of consumption factors and transfer coefficients for the mechanical−biological wastewater-treatment process. This material is available free of charge via the Internet at http://pubs.acs.org.

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