First estimation of occurrence and fate of organic substances in combined sewer systems with pollution load simulations

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Abstract

Emissions of selected organic substances from a hypothetical combined sewer system are calculated by pollution load simulation. The results are subsequently discussed. First, representative concentrations of chemical oxygen demand (COD), ammonium (NH4-N) and eight selected organics (polycyclic aromatic hydrocarbons (PAH), isoproturone, Di(2-ethylhexyl)phthalate (DEHP), ibuprofen, 17-β-estradiol (E2), 17-α-ethinylestradiol (EE2), ethylenediamine tetraacetic acid (EDTA), nitrilo triaceticacid (NTA)) in dry weather flow, surface runoff and effluent of WWTP in combined sewer systems are stated based on a literature survey. The second part of the paper presents pollution load simulations and first calculations of possible distributions of organics in combined sewer systems for a hypothetical catchment. Different scenarios of annual discharge loads of main emission matrices of the catchment (waste water treatment plant (WWTP) effluent and combined sewer overflow (CSO)) are compared to determine significant discharge points. The results of the pollution load simulations show that generally discharges from the WWTP dominate the total emissions of combined sewer systems. Nevertheless, emissions from CSOs are not negligible in some cases (e.g. for estradiol).

In summary, the results give first indications about possible strategies to reduce pollutant emissions from combined sewer systems. The paper also formulates recommendations for the selected organic compounds.

Keywords
combined sewer system, CSO, organic substances, pollution load simulation

INTRODUCTION

Emissions of combined sewer systems, especially CSOs, can affect receiving waters. In order to estimate the effects of these emissions, up to now predominately classical waste water parameters such as COD and NH4-N have been investigated. With the implementation of the EU-Water Framework Directive, which lists many organic compounds as priority substances in Annex X, investigations are beginning to focus on possible emissions out of combined sewer systems and their effects on receiving waters (Welker, 2004). There is insufficient data on organic compounds in the main flow types of combined sewer systems. In particular, no information about occurrence and distribution in the combined sewer systems is available.

Open Questions and Aim of the Study

This study gives a first evaluation of possible impacts of combined sewer system on the receiving waters by

- collecting available data of selected substances occurring in important flow types of the combined sewer system
- stating representative and preliminary concentrations in dry weather flow, surface runoff and effluent of WWTPs in combined sewer systems
- calculating annual discharge loads based on long term pollution load simulation for a hypothetical catchment and
• estimating tendencies of fate and distribution of selected compounds using different scenarios for the catchment (e.g. consideration of enhanced treatment).

METHODS

Literature survey

Selected organic substances, which are likely to occur in the combined sewer system, are described based on a literature survey considering over 300 citations (Welker, 2004). This paper discusses two classical waste water parameters (COD and NH₄-N) and eight selected organics (PAH, isoproturone, DEHP, ibuprofen, E2, EE2, EDTA and NTA).

The analysis of the results of field studies leads to a first estimation of representative concentrations in the flow types dry weather flow, surface runoff and WWTP effluent (see table 1). Deviations from the concentrations listed below are possible and occur. Nevertheless, they are estimated for the first time and can be used as input data for other studies. The criteria used for the estimation of the representative concentrations vary from substance to substance and between different matrices (see results).

Table 1. estimated substance concentrations in important flow types of the combined sewer system (input parameters for the pollution load simulation)

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<tbody>
<tr>
<td>dry weather flow</td>
<td>349</td>
<td>17</td>
<td>1.2</td>
<td>1.0</td>
<td>23</td>
</tr>
<tr>
<td>surface runoff</td>
<td>107</td>
<td>1.0</td>
<td>3.4</td>
<td>5.0</td>
<td>7.3</td>
</tr>
<tr>
<td>effluent WWTP (dw)</td>
<td>52</td>
<td>2.0</td>
<td>0.5</td>
<td>0.8</td>
<td>4.6</td>
</tr>
<tr>
<td>effluent WWTP (ww)</td>
<td>47</td>
<td>0.65</td>
<td>1.0</td>
<td>3.1</td>
<td>3.1</td>
</tr>
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<tbody>
<tr>
<td>dry weather flow</td>
<td>1,500</td>
<td>17</td>
<td>9</td>
<td>46</td>
<td>116</td>
</tr>
<tr>
<td>surface runoff</td>
<td>&lt; 2.0*</td>
<td>&lt; 0.025*</td>
<td>&lt; 0.025*</td>
<td>&lt; 0.05*</td>
<td>&lt; 0.05*</td>
</tr>
<tr>
<td>effluent WWTP (dw)</td>
<td>300</td>
<td>0.9</td>
<td>4.5</td>
<td>46</td>
<td>5.8</td>
</tr>
<tr>
<td>effluent WWTP (ww)</td>
<td>102</td>
<td>0.3</td>
<td>1.5</td>
<td>16</td>
<td>2.0</td>
</tr>
</tbody>
</table>

dw: dry weather; ww: wet weather; COD: chemical oxygen demand; NH₄-N: ammonium; PAH: polycyclic aromatic hydrocarbons; DEHP: diethylhexylphthalat; E2: estradiol; EE2: ethinylestradiol; EDTA: ethylenediamine tetraacetic acid; NTA: nitrilo triaceticacid; * calculation with 50 % of the lowest published detection limit

Pollution load simulations

Hypothetical catchment

Simulations were carried out for a hypothetical catchment (187 ha) with 9,900 inhabitants which has been used as representative catchment for various theoretical studies in Germany (Leinweber, 2002; Schmitt and Dittmer, 2002). The catchment has a total paved area of 98 ha and is drained by a combined sewer system including two CSOs (R10 and R30) and two storm water tanks (SWT) (B10 and B20) (for details see Welker, 2005). The overflow structures and the tanks are designed according to the German guideline A 128 (ATV, 1992).

Simulation Model

For pollution load simulation the KOSMO-model was applied (Schmitt, 1993). KOSMO includes submodels for all relevant processes like surface pollution with an exponential accumulation and washoff simulation. Surface runoff and corresponding sewer flow are computed using a hydrological method in this study. Storage and overflow devices are simulated accord-
ing to actual hydraulic conditions. Rain fall data of a one year period (825 mm/year), based on real data from a region in southwest Germany, was used.

Description of the scenarios
In comparison to scenario 0 (described below) further simulations were performed in order to observe possible changes in the load distribution when conditions are modified in the catchment. Different scenarios were designed in terms of (1) implementing enhanced treatment devices for the CSOs and the effluent of the WWTP, (2) connecting industrial dischargers to the catchment. Further scenarios (e.g. disconnection of paved areas) are described elsewhere (Welker, 2005).

Scenario 0. The computed annual volumes for the main emissions out of the catchment in the base scenario are: volume of CSO = 199,728 m³/year; volume of WWTP effluent (dry weather) = 1,498,837 m³/year; volume of WWTP effluent (wet weather) = 596,154 m³/year. Concentrations from table 1 were used as input data.

Scenario 3a. In scenario 3a the effect of enhanced treatment of CSOs with soil filters (SF) on total emissions of the system was analysed. For COD and NH₄-N a reasonably good data base for elimination capacity in SFs exists whereas no measurement data are available for organics (PAH, E2, EE2). Therefore assumptions based on substance properties were used for estimating the elimination capacity for these substances in the SFs.

Scenario 3b. In comparison to 3a, in this scenario effects of enhanced treatment on the WWTP were analysed. In order to do this, available effluent concentrations of selected substances (COD, NH₄-N, PAH, E2, EDTA) were collected from published WWTP monitoring programs. Out of these, the lowest measured effluent concentrations were selected. These conditions predominately occur on WWTPs with membrane facilities or other enhanced treatment devices (e.g. activated carbon filter).

Scenario 4. Possible variations by consideration of an indirect discharger in the catchment were investigated scenario 4. A single discharger with a high substance concentration was implemented in the hypothetical catchment. The conditions of this scenario represent a “worst-case” situation with an industrial discharger connected to an existing urban catchment.

RESULTS AND DISCUSSION

Literature survey
The results of measurement programs show a wide range of concentrations for various substances. The main reasons for this divergence are that conditions of field studies vary in terms of investigation methodologies, site specific factors and hydrological conditions (Welker and Schmitt, 2001; Welker, 2004).

COD. COD is an important chemical quality parameter in sewer systems and is therefore considered in various sewage-related regulations. An advantage of this parameter is the relatively easy determination which leads to a good data basis and provides a good transferability of data in different flow types. A disadvantage of COD and other sum parameters is that it is not possible to formulate statements on ecotoxicological effects. COD derives from, both dry weather flow and surface runoffs. The amount of COD transported with particles differs depending on the considered flow type (Welker and Schmitt, 2001).

Ammonium (NH₄-N). Ammonium is biodegradable in WWTPs to a very high extent and is transported predominately in the soluble phase. Toxicity effects are varying. While effects on humans are rather marginal, ammonium and especially the formed ammonia acts as a potent toxic substance on aquatic organisms, in particular fish. Being a nutrient, ammonium can also contribute to eutrophication effects on water resources. Because of this, ammonium limits can
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often be found in regulations considering receiving water quality. Concentrations in different flow types of the combined sewer system occur in a very wide range. Ammonium predominantly originates from dry weather flows (Welker, 2004). Monitoring programs observing ammonium pollution in CSOs have been conducted nearly to the same extent than those for COD (Brombach and Fuchs, 2002). In comparison to other organics the data base is therefore relatively satisfying.

**PAH.** Since some PAHs are regarded as a class of compounds with a carcinogenic potential, this parameter is listed in many regulations concerning drinking water and receiving waters. PAHs formation takes place mainly in incomplete combustion processes, the main sources are coke producing industries, household firing and vehicle traffic. Many PAHs are very hydrophobic and therefore transported predominately with particles and accumulated in solid matrices (soil, sewage sludge). In combined sewer systems, PAHs originate especially from surface runoffs (e.g. particles from asphalt and car exhaust in street runoff). Since PAHs are relatively well investigated in urban drainage systems and are of enormous environmental concern, they will remain an important water quality parameter in combined sewer systems (Haritopoulou, 1996).

**Di(2-ethylhexyl)phthalate (DEHP).** Phthalates, especially DEHP, are listed in various regulations (e.g. EC-Working document on Sewage Sludge and EU-Water Framework Directive). DEHP’s toxicity effects on humans are generally regarded as being rather low, but are also discussed controversially, whereas ecotoxic effects are regarded as being more relevant, predominately after sorption to receiving water sediments. Furthermore, several phthalates show first indications of endocrine effects (Helmreich, 2001). Phthalates enter the aquatic system by plastic industry processes (usage as plasticizer) and household contribution (e.g. diffuse extraction of rubber, plastics) (Litz et al., 1998; Umweltbundesamt, 1996). Therefore they can occur both in dry weather flow and surface runoff. Since phthalates are stated as ubiquitous substances, difficulties in analytical methods have been reported because of the formation of artefacts during the analysis (lab plastics). Due to minor water solubility and high solid adsorption capacity, DEHP is transported mainly in the solid phase in waste water systems. It is therefore primarily eliminated in WWTP by transfer into the sludge fractions (Kollotzek et al., 1998). Up to now, the relevance for urban drainage systems is difficult to estimate. On the one hand phthalates have a moderate to high biodegradability and on the other hand enormous quantities occur in the aquatic system.

**Isoproturon.** Isoproturon is one of the most commonly used herbicides in Germany and it is listed as a priority substance in the EU-Water Framework Directive. Predominately it occurs in the water phase and is not eliminated in WWTP (Nitschke and Schüssler, 1998). Since usage is related to the growth-period of crops, high quantities occur very seasonally in contrast to other mentioned substances. There is only little measurement data available for different flow types of combined sewer systems. Significant quantities of isoproturon might be found in CSO, when farm runoffs are connected to a combined sewer system. This has already been detected in Germany, especially in the southwest part, where combined sewer systems are very common and many homesteads exist. Here, cleaning of herbicide application devices on the farm surface is the source of high isoproturon amounts (Beudert, 1997). In these cases, CSO discharges can play an important role in contributing isoproturon emission to receiving waters. An overall estimation in Germany on contribution of pesticide sources already pointed out that farm runoffs may provide a significant impact on receiving waters (Bach et al., 2000).

**Ibuprofen.** Ibuprofen is a commonly used analgetic in human medication and is often detected in influents from WWTP and receiving waters (Thornton et al., 2001; Reinhard et al., 2003). It is stated as easily biologically degradable. Since many data on this substance can be found, especially in German literature, it has been chosen as an example of a substance which only derives from dry weather flow (Kalbfus, 1997). Furthermore the elimination in the WWTP is
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good (ca. 90 %). Toxic impacts on humans are well investigated whereas a lack of information about ecotoxicological effects still remains (Webb, 2001). Because of these uncertainties medical substances are not listed in water regulations up to now. Beside ibuprofen further pharmaceuticals can be found in combined sewer systems like antibiotics (e.g. erythromycin), further analgetics (e.g. diclofenac) and anti-neoplastic drugs (e.g. cyclophosphamide) (Heberer, 2002; Welker, 2004).

E2/ EE2. The natural hormone estradiol and the synthetic hormone ethinylestradiol show significant estrogenic effects on different aquatic organisms. They have been found in receiving waters and in effluents of municipal WWTPs (Birkett and Lester, 2003; Spengler et al., 2001). Due to a significant degradability estradiol is eliminated in WWTPs to a very high extent. Nevertheless concentrations measured in effluents reach values where estrogenic effects on fish cannot be ruled out. In influents of WWTPs estradiol was predominately found in the water phase (ATV-DVWK IG-5.4, 2002). In comparison to estradiol ethinylestradiol is more often detected related to particles in waste water samples and is eliminated to a lower degree in the WWTP (ATV-DVWK IG-5.4, 2002). Both, estradiol and ethinylestradiol, exclusively enter combined sewers through human excrements; there is no data on concentrations in CSOs available.

EDTA/ NTA. As complexing agents EDTA and NTA enter the combined sewer system predominately with the dry weather flow. Although coming from the same source their properties and behaviour in the waste water system are completely different. EDTA has a low biodegradability and is normally transported in the water phase. Therefore it is not eliminated during the waste water treatment process (LUA NRW, 2003). An amount of short and long term effect data is available related to receiving water organisms but the results are very heterogeneous. This is due to the different behaviour of various chemical forms of EDTA and the influence of different environment conditions (e.g. hardness) (CSTEE, 2003).

NTA, which has been used as a substitute for EDTA, is eliminated in WWTP up to 99 % mainly by biodegradation (Alder et al., 1997). Since it is also very soluble significant emissions out of the CSO devices are thinkable. Measurements in the CSO flow of both complexing agents are not available up to now.

Pollution load simulations

In figure 1 results of the long term pollution load simulation for the selected substances for the base scenario 0 are illustrated. The percentages of emitted annual loads, divided in CSO and WWTP (dw, ww) are shown. The importance of the single emissions differs significantly from substance to substance.

Figure 1. Percentage of annual pollution loads in scenario 0 from COD, NH4-N, PAH, isoproturone, DEHP, EE2, EDTA, ibuprofen, E2 and NTA calculated by pollution load simulation in a hypothetical combined sewer system
Substances that predominately originate from surface runoffs also occur in high quantities in CSO emissions. This was quantified by the example of PAH (ca. 30% of the pollution loads out of CSO). Furthermore, the relevance of the effluent of WWTPs during wet weather is demonstrated by the example of primarily surface runoff derived substances.

A completely different result is obtained for dry weather flow derived substances, like EE2. In contrast to PAH the percentage of CSO loads is negligible (ca. 3%). Main emissions come from the WWTP effluent, predominately during dry weather due to the relatively low elimination rate in the WWTP (ca. 50%). Therefore the origin of a substance (surface runoff or dry weather flow) is an important factor when considering quantities and distribution of pollution loads in a combined sewer system. However, the example of E2 shows that the origin is not the only factor. Similar to EE2, it predominately originates from dry weather flow. In contrast, annual loads from CSOs are not negligible (over 20%). This effect is caused by the very high elimination rate (up to 99%) in the WWTP.

In summary, an estimation of the distribution of the emissions from a combined sewer system needs information about the predominant origin (surface runoff, dry weather flow) and the elimination rate in the WWTP.

Besides the “standard” situation (scenario 0) it is interesting to investigate possible changes in the load distribution pattern when conditions are modified in the catchment.

This is an ideal application for a simulation model. Therefore, different scenarios were developed and computed with pollution load simulation model (see above); the results of three variations in comparison to scenario 0 are illustrated in figure 2. Analogous to what happened in the base scenario, the results for different substances varied considerably.

**Figure 2.** Emitted annual loads of COD, NH$_4$-N [kg/year], PAH, E2 and EDTA [g/year] calculated by pollution load simulations for a hypothetical combined sewer system

In *scenario 3a* effects of an enhanced CSO treatment by soil filters were simulated. With respect to the conditions of this scenario exclusively the CSO load can be reduced. Therefore effects on the total emitted loads are more significant in case of surface runoff derived substances like PAHs. Besides, annual loads of dry weather derived substances like NH$_4$-N and E2 are also reduced in this scenario. This is explained by the assumption of a high elimination rate in the soil filter. On the contrary, EDTA emission cannot be reduced significantly due to the minor relevance in CSO loads and the low retention capacity in the soil filter. Neverth-
less, the potential for reducing pollution loads for many substances in soil filters can be demonstrated.

Implementation of enhanced treatment on the WWTP and effects on the emitted pollution loads were the focus of scenario 3b. In comparison to scenario 3a changes are only observable in the annual WWTP loads. Since these are relevant for all substances the reduction potentials on the total emissions are very significant in this scenario.

In scenario 4 consciously unrealistic conditions were chosen in order to represent a situation with “worst case” emissions. This was done by implementing a large discharger in the hypothetical catchment (see above). Under these conditions total pollution loads of all substances increase significantly. The results highlight the possible importance of single industrial dischargers in urban catchments. In order to reduce total emissions, in these cases a pretreatment before discharging to the sewer system is recommended.

Certainly this and other statements predominately apply for the observed catchment with the conditions of the examined scenario. Nevertheless a relative comparison is feasible and first conclusions about the tendency of variances can be drawn.

CONCLUSIONS

A main conclusion of this investigation is the necessity for a broader data base on the quantities of organic substances in the matrices of combined sewer systems and for the CSOs in particular. Besides the introduced substances, further compounds (e.g. personal care products, flame retardants) should be taken into account with respect to the occurrence and behaviour in the combined sewer system.

Furthermore it is shown, that emissions from CSOs are not negligible, surprisingly also for substances, that originate from dry weather flow with a high removal capacity in the WWTP. Therefore it cannot be excluded that pollution emissions from CSOs cause adverse effects in receiving waters.

Further studies on pollution load simulations will consider additional organic substances and variations in the catchment structure, a scenario which is likely these days. Here the integration of separate sewer systems and the implementation of new treatment facilities are possible solutions.

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