Meta-Analysis of Mass Balances Examining Chemical Fate During Wastewater Treatment

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Supplemental Information

Sampling strategies employed

Tracking the mass flow of OWCs during sewage treatment requires sampling strategies for both wastewater and sewage sludge. The selection of appropriate sampling methodologies is driven in part by the treatment approach utilized. Mass balances conducted to date at municipal WWTPs have concentrated exclusively on activated sludge treatment facilities that, with only two exceptions (1), utilized anaerobic digesters for sludge processing.

Sampling of wastewater

All studies reviewed herein included sampling and analysis of raw sewage (influent) and final effluent. Depending on the specific treatment train, one or more of the following additional matrices were sampled: primary treatment effluent, secondary treatment effluent, sequential batch reactor effluent, trickling filter effluent, and microfiltration/reverse osmosis effluent. To obtain composite samples representative of daily mass flow, studies commonly relied on flow-proportional (2-7) and time proportional (8-11) automated sampling over a period of 24 hours. To reveal intra-day variation, three studies also collected hourly samples (10,11) and 8-hour composite samples (3). Grab sampling of aqueous process streams has been utilized only occasionally due to its inherent limitations (1,12).

Sampling periods varied, ranging from 2 – 10 consecutive days (5,13) to several sampling events over a longer period of 4 – 16 months (6,12). One study design involved 4 sampling events on 3 consecutive days over a period of 7 months (13).

Sampling of sewage sludge

For practical considerations, all studies reviewed relied on grab sampling for the collection of sewage sludge regardless of whether batch or continuous-flow processes were investigated. All
studies involved an examination of the end product of solids treatment, mostly consisting of anaerobically digested sludge. Additional samples collected from different unit operations included: primary sludge, return activated sludge, waste activated sludge (excess sludge), thickened sludge and pelletized sludge. Sampling of sludges and liquids typically were performed in parallel (2,4-6,8-11). In one study, digested sludge was obtained 20-25 days after the wastewater samples were obtained to take the residence time of the digester into account (3). The number of sampling events varied among studies from one-time sampling (5) to several consecutive days (8,9) to once every several month (1).

Sample preparation techniques utilized
Aqueous samples and solid samples, including sewage sludge and wastewater particulates separated from liquid samples, are different matrixes requiring distinct processing techniques (Table S1).

Processing of aqueous samples
Cleanup of wastewater influent and effluent samples typically is comprised of one or a combination of the following approaches: a separation step to remove suspended solids from the aqueous phase, pH adjustment, analyte extraction and further cleanup procedures. Removal of suspended solids is usually done via filtration or centrifugation. The separated solids either are discarded (2) or subsequently processed and analyzed to obtain a more complete mass balance (5). Filtering of liquid samples prior to analysis enables use of solid phase extraction (SPE) without running the risk of clogging the SPE cartridge but it severely diminishes the value of the results obtained. In contrast, liquid/liquid extraction can capture the entire analyte mass of a sample in a single step (8,9). An optional pH adjustment can be performed prior to extraction for compounds such as fluoroquinolones (2,4) and nonylphenols (1). Most commonly SPE is used for the concentration of target analytes in aqueous samples.
Depending on the chemical properties or class of target analytes, several types of SPE cartridges are used (Table S1). After analyte elution, resulting organic extracts are usually evaporated under a stream of nitrogen or in a rotary evaporator. Additional cleanup methods used for the detection of synthetic musks (13) and estrogens (5) are silica gel columns and gel permeation chromatography. Given sufficiently high analyte concentrations, a completely different approach also has been employed involving centrifugation of the samples followed by direct injection of large-volume aqueous samples into the detection system without any prior concentration step (14).

Processing of solids
Solids comprise particulates separated from wastewater and sludge samples. Compared to aqueous samples, the cleanup of solid samples is more difficult due to the inherent complexity of this sample matrix. Co-extraction and co-elution of impurities is known to interfere with both analyte detection and quantification. Therefore, sample extraction and cleanup conditions have to be chosen carefully to minimize such undesirable effects.

Generally, the methods employed consist of drying of samples, followed by liquid extraction and optional cleanup steps. Sludge and particulate samples were either air dried at ambient or elevated temperature in an oven or freeze dried. Three extractions techniques were used: (i) solid/liquid extraction using a shaker or sonicator (2,5,7,10-12); (ii) accelerated solvent extraction (ASE), which utilizes high temperatures and pressurized organic solvents to enhance extraction efficiencies (1,3,4,6,13); and (iii) Soxhlet extraction, i.e., extended boiling of sampling materials with reflux of condensate (8,9). Extraction solvents were chosen according to the polarity of the target analyte and ranged from 75% aqueous to 100% organic as a mixture of equal parts of hexane and ethyl acetate. Further cleanup steps comprised the use of gel permeation chromatography (GPC) (5,8,9,13), silica gel chromatography (5,13) and SPE (3,4,6-9).
Detection methods employed
Several methods were employed to detect the target analytes (Table S1). To chromatographically resolve analytes and interferences, sample extracts were injected into either high pressure liquid chromatography (HPLC) or gas chromatography (GC) systems connected online to a detector. The chromatography methods used were depended on the physical and chemicals properties of the analytes. For example, very hydrophobic estrogens or synthetic musks were chromatographically resolved using GC (5,13), whereas more hydrophilic targets were separated by LC (6). Additionally, estrogens were derivatized prior to analysis and detected as the respective trimethylsilyl- (1) and pentafluoro-benzyl-trimethylsilyl derivatives (12). Most commonly the chromatography systems were coupled to mass spectrometers (MS). Depending on the instrument, analytes were detected in selective ion monitoring (SIM) mode (10) or, if the instrument had tandem MS capabilities, in selective reaction monitoring (SRM) mode (3). Other methods of detection were fluorescence detection (FLD) (1,4), and diode array detection (DAD) (1).

Methods of quantification used
Most studies reviewed used surrogate standards added upfront in sample preparation (Table S1). Standards used were either stable isotope labeled analogs of target analytes (10), structural analogs (2), or related compounds not found in the various matrices under investigation (1). Some studies relied on the addition of an internal standard just prior to analysis (10). One study used a surrogate standard approach for analysis of aqueous samples and an internal standard added just prior to analysis of extracts from sample solids (2). Less frequently used quantification approaches were standard addition (6) and external calibration (13).
Mass balance calculation approaches

Generally, a mass balance can be described as a method to measure mass flows entering and leaving a system. In terms of wastewater treatment, this concept can be applied by determining the mass of a chemical entering the plant in raw wastewater, and the mass that exits the plant contained in treated wastewater, sewage sludge or both. A simple scheme for a mass balance is shown in equation S-1.

Equation S-1

\[ M(i)_{\text{enter}} = M(i)_{\text{exit}} + M(i)_{\text{lost}} \]

with \( M(i)_{\text{enter}} \) being the mass of chemical \( i \) entering the plant (mass/time), \( M(i)_{\text{exit}} \) the mass of chemical \( i \) leaving the plant (mass/time) and \( M(i)_{\text{lost}} \) (mass/time) the mass of chemical \( i \) being degraded or lost. A mass balance approach can be conducted for a plant as a whole (8,10), and/or for each unit operation of the entire treatment train (7,13). To obtain a mass balance for a WWTP or treatment step, measured concentrations of a target analyte have to be multiplied with the respective volumetric flow to yield mass flow per unit time. Therefore, the wastewater or sludge flow of each sampling location needs to be known for the time of sampling. The mass of a chemical dissolved in the aqueous phase can be calculated with equation S-2,

Equation S-2

\[ M(i)_{\text{diss}} = Q \times C(i)_{\text{aq}} \]

where \( M(i)_{\text{diss}} \) is the mass of chemical \( i \) dissolved in the aqueous phase (mass/time), \( Q \) equals the flow of wastewater (volume/time), and \( C(i)_{\text{aq}} \) the measured concentration of chemical \( i \) in the aqueous phase (mass/volume). To obtain the mass of an analyte sorbed to particles, the suspended solids content needs to be taken into account as either concentration (mass/volume) or as a fraction of the total flow as shown in equation S-3,
Equation S-3  \[ M(i)_{\text{sorb}} = Q \times C(i)_{\text{sorb}} \times S \]

where \( M(i)_{\text{sorb}} \) is the mass of chemical \( i \) sorbed to suspended solids (mass/time), \( Q \) the total flow (volume/time), \( C(i)_{\text{sorb}} \) the concentration of chemical \( i \) measured in solids (mass/volume or mass/mass) and \( S \) the suspended solids content (% or mass/volume). Equations S-2 and S-3 can be used to develop a mass balance for a complete WWTP as shown in equation S-4.

Equation S-4  \[ M(i)_{\text{inf/diss}} + M(i)_{\text{inf/sorb}} = M(i)_{\text{eff/diss}} + M(i)_{\text{eff/sorb}} + M(i)_{\text{sludge/sorb}} + M(i)_{\text{lost}} \]

Most of the reviewed papers applied this approach. However, not all authors present a description of their approaches. Also, some authors sum up the mass of dissolved and sorbed analytes (7,10,11), while others present the mass of dissolved and sorbed analyte separately (2,5,6). A different approach to determining the mass of analyte sorbed to particulates is by estimation. One study estimated the sorbed mass of analyte in primary effluent from the measured mass in raw sewage by assuming primary effluent contains 30% of raw sewage solids (4). A different approach to estimate the sorbed mass in influent and primary effluent was taken by using the partition coefficient (\( K_D \)) and suspended solids concentration (3). Additionally, to compare mass flows of two plants, the same study normalized the mass balance for the size of the population served (3).
Table S1. Summary table of compounds targeted and methods used in mass balance studies considered in this review.

| Reference | Compound | Sampling | Aqueous | Solids | Quantification | Detection |
|-----------|----------|----------|---------|--------|----------------|-----------|
| Andersen; 2003 (5) | Estrone 17β-Estradiol 17α-Ethynylestradiol | Aqueous: 24 hour flow proportional composite; 2 consecutive days | Filtration SPE (C-18) Silica gel column GPC (for influent) | Freeze drying 2 x methanol extraction 2 x acetone extraction GPC Silica gel column | Surrogate standard: (17β-estradiol-17-acetate) Internal standard: Mirex | Derivatization (trimethylsilyl) GC-MS |
| Braga; 2005 (12) | Estrone 17β-Estradiol 17α-Ethynylestradiol | Aqueous: duplicate grab samples; weekdays over 4 month taken | Filtration SPE (C-18) | Freeze drying Hexane:acetone (50:50) extraction | Isotope labeled surrogate standard (d4-E1) | Derivatization (pentafluoro-benzyl-trimethylsilyl) GC-MS |
| Bester; 2003 (8) | Triclosan | Aqueous: 2h interval 24 h composite; 5 consecutive days | Liquid-liquid extraction (toluene) | Freeze drying Soxhlet extraction (ethyl acetate) SPE (silica) GPC | Surrogate standard: (d15-musk xylene) | GC-MS |
| Heidler; 2006 (11) | Triclosan | Aqueous: Hourly time proportional for 24 h + 24 composite for 7 consecutive days | Centrifugation SPE (Oasis HLB) | Drying Methanol:acetone (50:50) extraction | Isotope labeled surrogate and internal standard (13C6-triclosan, d7-triclocarban) | LC-MS |
| Heidler; 2006 (10) | Triclocarban | Aqueous: Hourly time proportional for 24 h + 24 composite for 7 consecutive days | Centrifugation SPE (Oasis HLB) | Drying Methanol:acetone (50:50) extraction | Isotope labeled surrogate and internal standard (13C6-triclocarban, d7-triclocarban) | LC-MS |
| Authors       | Compounds            | Plants | Aqueous Sampling          | Sludge Sampling                  | Filtration Methods                                      | Drying Methods                                      | Surrogate Standards                                      | LC/MS Methods     |
|--------------|----------------------|--------|---------------------------|----------------------------------|----------------------------------------------------------|-----------------------------------------------------|----------------------------------------------------------|-------------------|
| Goebel, 2005 (3) | Sulfamethoxazole, Trimethoprim, Clarithromycin | 2      | flow proportional composite over 2 or 3 days + 8 hour composite over 3 consecutive days; Plant 1: 3 times in 20 month; Plant 2: 2 times in 8 month. | Sludge: grab; 20-25 days after aqueous sampling | Filtration (Oasis HLB) | Freeze drying, ASE (methanol:water 50:50) | Isotope labeled and non-labeled surrogate standards (sulfamethoxazole-d4; Sulfamethazine-phenyl-$^{13}$C$_6$; tylosin) | LC-MS/MS          |
| Golet; 2003 (4)   | Ciprofloxacin, Norfloxacin |        | Aqueous: 24 hour flow-proportional; 7 consecutive days               | Sludge: grab; multiple times over 22 month | Filtration (Acidification SPE (mix-phase cation exchange)) | Drying ASE SPE (mix-phase cation exchange) | Surrogate standard: (Tosulfloxacin)(17) | LC-FLD             |
| Lindberg; 2006 (2) | Ciprofloxacin, Norfloxacin, Trimethoprim |        | Aqueous: 24h flow-proportional composite; 3 consecutive days; only 1 influent sediment sample | Sludge: grab, 3 consecutive days | Filtration Acidification (pH 3) SPE (ENV+) | Drying Phosphate buffer (pH 6) extraction 5%TEA in methanol:water (25:75) extraction | Surrogate standards (aqueous) and internal standards (solids) (Enrofloxacin; Diaveridine) (18) | LC-MS/MS          |
| Keller; 2003 (1)  | Nonylphenol          | 3      | Aqueous: grab; 4 times from early                                     | Filtration Acidification (pH 2) SPE (C18) | Freeze drying ASE (hexane:acetone 1:1) | 4-t-butylphenol Internal standard addition: | GC-MS            |
| Author       | Year  | Compounds                  | Sample Handling | Extraction | Cleanup | Detection | Solvent/Condition                  | Additional Details |
|------------|-------|---------------------------|-----------------|------------|---------|----------|-----------------------------------|--------------------|
| Miao;      | 2005 (6) | Carbamazepine             | Aqueous: 24 hour flow-proportional composite; 2 times in 4 month | Filtration SPE (Oasis HLB) | Centrifugation ASE (acetone:water 3:7) SPE (Oasis HLB) | Standard addition | LC-MS/MS                        |                     |
|            |       |                           | Sludge: grab; 1 day |            |         |          |                                   |                     |
| Schultz;   | 2006 (7) | Perfluoroalkyl sulfonates | Aqueous: 24 hour flow-proportional composite; 10 consecutive days | Centrifugation Direct injection into analysis system | Drying Acetic acid wash 2 x methanol:water (90:10) + 1% acetic acid extraction SPE (C-18) (19) | Isotope labeled and non-labeled internal standards: perfluoro(2-ethoxyethane) sulfonic acid (PFES) [1,2,13C2] perfluoro-ocanoic acid (13C2-PFOA) 2-perfluoroctyl[1,2,13C2]ethanoic acid (MFOEA) (14,19) | LC-MS/MS            |                     |
|            |       | Perfluoroalkyl carboxylates |                       |            |         |          |                                   |                     |
|            |       | Fluoroalkyl sulfonamides  |                       |            |         |          |                                   |                     |
|            |       | Fluorotelomer sulfonates  |                       |            |         |          |                                   |                     |
| Yang;      | 2005 (13) | HHCB AHTN                 | Aqueous: composite samples; 4 times in 9 month over 3 consecutive days | Filtration 2 x hexane extraction GPC | Centrifugation ASE (hexane/ethyl acetate 1:1) GPC | External Calibration | GC-MS                           |                     |
|            |       |                           | Solids: grab, same time as aqueous |            |         |          |                                   |                     |
| Bester;    | 2005 (9) | HHCB AHTN                 | Aqueous: 2h interval 24 h composite; 5 consecutive days | Liquid-liquid extraction (toluene) | Freeze drying Soxhlet extraction (ethyl acetate) SPE (silica) GPC | Surrogate standard: (d15-musk xylene) | GC-MS                           |                     |
|            |       |                           | Solids: grab; 5 consecutive days |            |         |          |                                   |                     |
Fitting of plant performance data in the meta-analysis

For the meta-analysis, data on the fate of organic wastewater compounds (OWCs) examined in published mass balance studies were plotted on scatter plots and analyzed with Microsoft Excel. Studies published prior to February 2007 were considered in this task along with original work performed by that date. Information on the fraction of the total chemical loading persisting in digested sludge (Figure 3; panels A and B) was fit to a simple model (Equation 2) that produced an S-shaped curve when the data were plotted against log $K_{OW}$ and log $K_{OC}$, respectively. Use of equation 2 required fitting of the dimensionless parameter $p_{OC}$, which was accomplished by using the “Solver” function of Microsoft Excel. The best possible fit for $p_{OC}$ was obtained by minimizing the error. The correspondent values for $p_{OC}$ are reported in the body of the manuscript.

Equation 2 can be derived by considering the dissolved and sorbed fraction of a compound in a system containing suspended solids. The fraction of a compound in solution in this scenario has been defined as (20):

Equation S-5 \[ f_W = \frac{1}{1 + r_{SW} \cdot K_D}, \]

where $f_w$ is the fraction of a given compound dissolved in water, $r_{SW}$ is the soli-to-water phase ratio (e.g., kg/L), and $K_D$ is the solid-water partition coefficient. The fraction of a compound in solids ($f_S$) is defined as (20):

Equation S-6 \[ f_S = 1 - f_W. \]

Substituting for $f_W$ in Eq. S-6 using the relationship shown in equation S-5 yields:
**Equation S-7**  
\[ f_s = 1 - f_w = r_{SW} * K_D / (1 + r_{SW} * K_D). \]

Assuming that sorption is dominated by organic carbon as the principal sorbent, the partition coefficient can be defined as:\( (20) \):

**Equation S-8**  
\[ K_D = f_{OC} * K_{OC}, \]

where \( f_{OC} \) is the organic carbon content of the solids (dimensionless fraction).

Substituting for \( K_D \) in Equation S-7 using the relationship shown in Eq. S-8 yields:

**Equation S-9**  
\[ f_s = f_{OC} * r_{SW} * K_{OC} / (1 + f_{OC} * r_{SW} * K_{OC}). \]

To simplify the above expression, it is convenient to define a dimensionless fitting parameter (\( p_{OC} \)):

**Equation S-10**  
\[ p_{OC} = f_{OC} * r_{SW}. \]

Finally, substituting \( p_{OC} \) for \( f_{OC} * r_{SW} \) in Eq. S-9 yields:

**Equation S-11**  
\[ f_s = p_{OC} * K_{OC} / (1 + p_{OC} * K_{OC}). \]

This relationship, stated in more general terms in Eq. 2, served as the basis for data fitting. The approach also is applicable to \( K_{OW} \). In contrast, since the term overall persistence encompasses chemical mass in both the dissolved and sorbed state, the data shown in panel C of Figure 3 were evaluated by linear regression.
**K\textsubscript{OW} and K\textsubscript{OC} data**

Values of K\textsubscript{OW} and K\textsubscript{OC} were used to parameterize the sorption behavior of organic wastewater compounds. In the few instances where measured data were not readily available from the published literature, appropriate values were estimated using KOWWIN v1.67 (K\textsubscript{OW}) and Advanced Chemistry Development (ACD/Labs) Software v8.14 for Solaris, assuming standard conditions. It should be noted that reported values can vary substantially between both experimentally determined and estimated values for one and the same chemical. Deviations can result from, for example, the conditions employed or assumed, the experimental protocol used, the type of organic carbon studied (e.g., dissolved or particulate) and the theoretical model selected (21,22).

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