Chemosphere 138 (2015) 874–882

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

A comprehensive substance flow analysis of a municipal wastewater and sludge treatment plant

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HIGHLIGHTS

- Substance flow analysis was conducted at a municipal wastewater treatment plant.
- Fate of TOC and 32 inorganic constituents was identified at the unit process level.
- Conventional treatment process found to reduce toxic potential of wastewater.

ARTICLE INFO

Article history:
Received 20 June 2013
Received in revised form 11 September 2013
Accepted 17 September 2013
Available online 11 November 2013

Keywords:
Wastewater
Sewage sludge
Substance flow analysis
Heavy metals
Organic pollutants

ABSTRACT

The fate of total organic carbon, 32 elements (Al, Ag, As, Ba, Be, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, N, Na, Ni, P, Pb, S, Sb, Se, Sn, Sr, Ti, V, and Zn) and 4 groups of organic pollutants (linear alkylbenzene sulfonates, bis(2-ethylhexyl)phthalate, polychlorinated biphenyl and polycyclic aromatic hydrocarbons) in a conventional wastewater treatment plant were assessed. Mass balances showed reasonable closures for most of the elements. However, gaseous emissions were accompanied by large uncertainties and show the limitation of mass balance based substance flow analysis.

Based on the assessment, it is evident that both inorganic and organic elements accumulated in the sewage sludge, with the exception of elements that are highly soluble or degradable by wastewater and sludge treatment processes. The majority of metals and metalloids were further accumulated in the incineration ash, while the organic pollutants were effectively destroyed by both biological and thermal processes. Side streams from the sludge treatment process (dewatering and incineration) back to the wastewater treatment represented less than 1% of the total volume entering the wastewater treatment processes, but represented significant substance flows. In contrast, the contribution by spent water from the flue gas treatment process was almost negligible. Screening of human and eco-toxicity by applying the consensus-based environmental impact assessment method USEtox addressing 15 inorganic constituents showed that removal of inorganic constituents by the wastewater treatment plant reduced the toxic impact potential by 87–92%.

1. Introduction

Municipal wastewater is known to contain pollutants such as heavy metals and trace organic compounds from household and industrial sources (Wilkie et al., 1996; Sörme and Lagerkvist, 2002). Each pollutant is present in wastewater and sludge in a variety of forms: dissolved, exchangeable, attached to organic matters, occluded or co-precipitated with oxides, as carbonates and phosphate, ion crystals, and assimilated in biomass (Sterritt and Lester, 1984; Stasinakisa and Thomaidisb, 2010). The particulate portions of pollutants are removed through physical separation processes, though the fractionation of pollutants is affected by chemical and biological activities taking place simultaneously during wastewater and sludge treatment (Ziolko et al., 2011).

The concentration of pollutants in sludge is one of the important factors determining the end use of sewage sludge. During the last 40 years, the occurrence and fate of heavy metals, namely Cd, Cr, Cu, Hg, Ni, Pb, and Zn, in conventional wastewater treatment processes have been studied extensively. As classified by Santos and Judd (2010), the fate of pollutants is affected by many factors: plant operational parameters (sludge age, hydraulic retention time, and dissolved oxygen concentration), physicochemical parameters of pollutants (metal type, species, concentration, metal salts solubility, pH, concentration of chelating agents, and particle size), and biochemical sludge parameters (cell property and extracellular polymeric substances concentration). Yet, the results have

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http://dx.doi.org/10.1016/j.chemosphere.2013.09.045

consistently suggested that the majority of metals are present in the particulate phase of wastewater and, hence, accumulated in sewage sludge through physical separation such as sedimentation, thickening, and dewatering processes (Lester, 1983; Goldstone et al., 1990a,b,c; Chipasa, 2003; Busetti et al., 2005; Buzier et al., 2006; Da Silva Oliveira et al., 2007; Ustun, 2009; Stasinakisa and Thomaidisb, 2010).

Despite the abundance of knowledge on the fate of metals currently regulated by environmental protection laws such as As, Cd, Cr Cu, Pb, Hg, Ni, and Zn, little has been documented about the fate of other metals and metalloids through wastewater and sludge treatment processes, albeit some metals and metalloids such as Ag, Ba, Be, Sb, Se, and Ti are reported to have harmful effects on human and ecosystem health (ATSDR, 2002, 2007, 2009a,b,c; Haye et al., 2007; Rosenbaum et al., 2011). Munoz et al. (2008) ranked the potential impacts of 98 priority and emerging pollutants in urban wastewater using toxicity characterization methods for Life Cycle Assessment (LCA) and the results suggest that 10 out of 16 substances with high impact were currently unregulated. It is necessary to expand knowledge of the behavior of pollutants in wastewater treatment plants in order to capture the full extent of the benefits that wastewater treatment plants provide.

Another knowledge gap is related to the behavior of pollutants at the unit process level. Existing studies focus on the removal of pollutants at the plant scale by comparing the pollutant load in the influent to the wastewater treatment plant to the effluent from the plant. Many studies overlook the impact of internal recycling of materials from sludge treatment back to the wastewater treatment plant. These side streams generally represent 1–2% of the flow entering the wastewater treatment processes, but could contain significant amounts of substances. For instance, 20–50% of P passing through wastewater treatment processes is introduced with the reject water from the sludge treatment process (Shu et al., 2006; Van Loosdrecht and Salem, 2006). Only a few studies have characterized the behavior of pollutants at the unit process level and provided an overall picture of substance flows through wastewater and sludge treatment processes. Yet they tend to be dedicated to single elements or substances and do not provide an overall picture of pollutants' behavior (Prats, 1997; Karvelas et al., 2003; Balogh and Nollet, 2008).

This study provides a comprehensive overview of substance flows through wastewater and sludge treatment processes and identifies the substances of importance in terms of potential toxic effect on human health and ecosystems. Substance flow analysis of total organic carbon and 32 additional elements was conducted on the wastewater and sewage sludge treatment processes in a conventional wastewater treatment plant in Denmark. Four groups of organic pollutants (linear alkylbenzene sulfonate (LAS), bis(2-ethylhexyl)phthalate (DEHP), polychlorinated biphenyl (PCBs) and polycyclic aromatic hydrocarbons (PAHs)) were also included in the assessment, as they are regulated under Danish regulations on land application of sewage sludge. The substance flow of each constituent was constructed based on a static mass balance approach. The relative importance of each element was evaluated by combining the mass flows and toxicity potentials provided by the consensus-based human and eco-toxicity assessment model, USEtox (Rosenbaum et al., 2011).

2. Material and methods

2.1. Plant description

The Avedøre wastewater treatment plant (AV WWTP) is located south of Copenhagen, Denmark. Annually, the AV WWTP treats 25.3 million m^3 of wastewater generated by 265 000 inhabitants. About 85% of the wastewater is of domestic origin and the rest is from the industrial sector. The major industry served is small scale food processing and pharmaceutical plants. The service area of the AV WWTP is approximately 8000 ha. 17.5% of the service area has a combined sewer system, which contributes to large fluctuations in the influent flow volumes. In 2011, the daily influent volume varied from 30 000 to 219 000 $m^3\ d^{-1}$. Characteristics of influent and effluent are summarized in Table 1.

Fig. 1 presents a schematic diagram of the AV WWTP. The wastewater influent first goes through a preliminary treatment step where large objects are removed by screens; sand and grit are settled out in the grit chambers. From these grit chambers, fat and grease are skimmed off. This fat and grease is then mixed with warm digested sludge, and sent to anaerobic digesters. The wastewater proceeds through the grit removal process where it is then subjected to primary sedimentation. Effluent from the primary clarifiers is sent to a secondary treatment process which utilizes a biological N removal process (BioDeNitro configuration). Removal of N is optimized by on-line measurement-based control (STAR® control) system (Rosen et al., 2006). During this process, P is also partially removed by incorporation to microbial biomass but to comply with the Danish P discharge limits, ferric chloride sulfates is added to the effluent from biological treatment to precipitate the dissolved P. Effluent from the secondary clarifiers is sent to Køge bay about 1 km away from the plant. The operational parameters of the AV WWTP are summarized in Table 1.

Primary and secondary sludge is pumped to three mesophilic anaerobic digesters, each with a hydraulic retention time of 21 d. The generated biogas is utilized for electricity and heat consumption on site. Digested sludge is dewatered by a centrifuge and the dewatered sludge is dried using the heat recovered from a subsequent sludge incineration process. The dried sludge is sent to a fluidized bed incinerator with an operating temperature of approximately 950 °C. The flue gas from the incinerators is treated by electrostatic precipitators, bag filters with activated carbon and lime injection, quenchers and scrubbers. Treated wastewater is used as cooling water for the flue gas treatment and drying process. Ashes from the electrostatic precipitators and bag filters are deposited in an on-site disposal site. Warm spent water from the incinerator is mixed with reject water from the dewatering process and sent to the inlet of the treatment plant.

2.2. Sampling and analysis

Sampling campaigns were scheduled over 10 weeks starting September 30th 2011. In total 120 samples were taken from 12 different sampling points in the AV WWTP, which are indicated as tick marks in Fig. 1. A 24-h (7:00 am–7:00 am) flow proportionate composite sample of influent (IN), influent to aeration basin (InAB) and effluent (EF) were collected by refrigerated automated samplers. Grab samples of primary sludge (PS), secondary sludge (SS), fats, oils, and grease (FOG), digested sludge (DS), dewatered

Table 1
Average influent and effluent quality of the Avedøre WWTP in 2011.

	Unit	Influent	Effluent	Removal rate
Daily flow rate	$m^3\ d^{-1}$	83 656	80 895	–
COD	$mg\ L^{-1}$	529	29.3	94.5%
BOD	$mg\ L^{-1}$	204	2.92	98.6%
NH4-N	$mg\ L^{-1}$	35.7	0.867	–
NOx-N	$mg\ L^{-1}$	0.465	3.13	–
Total-N	$mg\ L^{-1}$	50.4	5.31	89.5%
Total-P	$mg\ L^{-1}$	8.45	0.60	92.8%
Suspended solids	$mg\ L^{-1}$	261	8.37	96.8%
pH	–	7.74	8.07	–

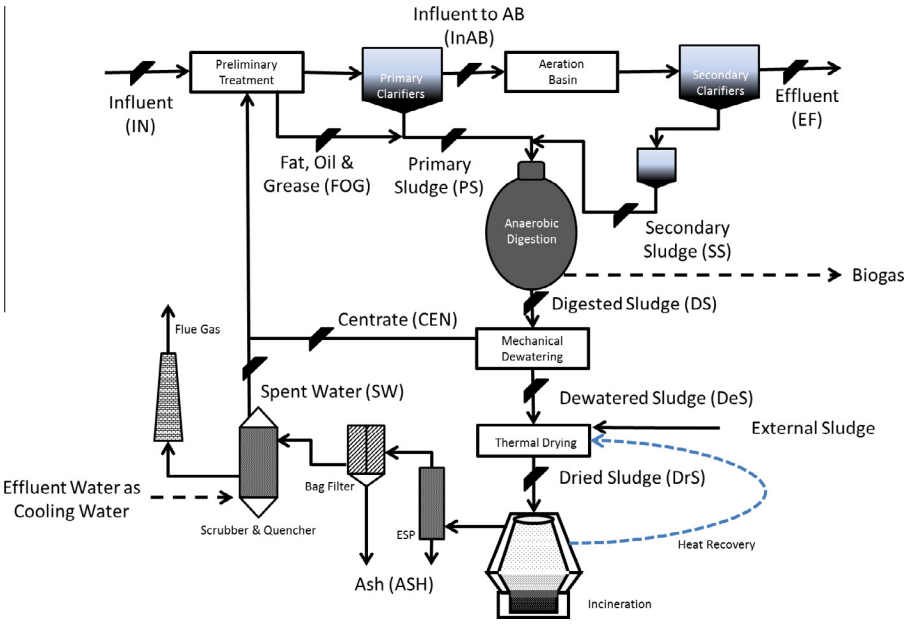

Fig. 1. Schematic diagram of the process configuration at Avedøre Wastewater Treatment Plant, Denmark. The tilted trapezoid indicates where samples were taken.

sludge (DeS), dried sludge (DrS), ash (ASH), centrate (CEN), and spent water from the flue gas treatment process (SW) were collected. Mass and volume flow data were collected daily by the supervisory control and data acquisition system installed at the AV WWTP.

Acid-washed wide mouth polypropylene bottles were used for samples targeting macro-constituents and trace metals, and dark glass bottles were used for sample analysis of trace organics. Total solids and volatile solids were analyzed following EPA method 2540 and measured within 24-h of sampling. Samples from alternate weeks were grouped. In total, two sets of five samples per each sampling point were mixed in proportion to their mass flow. In total, two sets of 12 flow proportionate samples were prepared. During the preparation period, samples were kept refrigerated (4 °C) and then frozen until further analysis.

Samples were analyzed at a certified lab (ALS Scandinavia Lab A/S) for total organic carbon (TOC), 32 elements (Al, Ag, As, Ba, Be, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, N, Na, Ni, P, Pb, S, Sb, Se, Sn, Sr, Ti, V, and Zn) and 4 groups of organic pollutants (linear alkylbenzene sulfonates (LAS), bis(2-ethylhexyl)phthalate (DEHP), polychlorinated biphenyl (PCBs) and Polycyclic aromatic hydrocarbons (PAHs)). 16 priority USEPA PAHs were considered in this study; C_{10}–C_{14} alkyl homologues for LAS; and 7 congeners (#28, 52, 101, 118, 138, 153, and 180) for PCBs.

Water samples of 12 mL (IN, InAB, EF, VEN, and SW) were digested with 1.2 mL of nitric acid in an autoclave. For Ag and Se analysis, HCl was used instead of nitric acid. Sludge samples (FOG, PS, SS, DS, DeS, and DrS) were digested in sealed Teflon containers with 5 mL of nitric acid and 0.5 mL of hydrogen peroxide. Ash samples were melted with lithium meta-borate followed by dissolution in dilute hydrochloric nitric acid. The elemental composition was measured by inductively coupled plasma atomic emission spectroscopy (EPA method 200.7) and TOC by CSN EN 1484. Mass spectrometry and gas chromatography were used to analyze PAHs, PCBs, and DEHP (EPA method 8061A, EPA method 8082), whereas High Performance Liquid Chromatography with Post column Fluorescence Derivatization was used for LAS (EPA method 531.1). C and N losses in biogas were calculated based on the operational data for biogas utilization. Analysis of flue gas for Cd, Hg, Pb and the sum of 9 heavy metals had been measured routinely once per year. Other gaseous emissions were calculated based on the mass balance of the measured values.

2.3. Data analysis

Mass flows of various constituents were calculated by multiplying the measured concentration in a given stream by the daily flow of total solids. In this study, uncertainty ranges were represented as standard errors of sample means. The STAN (subSTance flow ANalysis) model developed by the Vienna University of Technology was used to conduct substance flow analysis. STAN calculates the best fitted values iteratively using a successive linear data reconciliation process and the Gauss' Law of error propagation (Cenic and Rechberger, 2008). The standard uncertainty was calculated by combining the standard uncertainty for the following factors: variation in mass flow rate, total solid content, concentration of each element per mass of total solids, and accuracy of measurements.

2.4. Calculation of toxic impact potentials

Toxic impact potentials to human and ecosystems were calculated by assigning distinctive characterization factors to emissions of metals and metalloids in each environmental compartment. Characterization factors were calculated by the USEtox model. The USEtox model combines transport and fate models with empirical exposure toxic impacts for each pollutant (Rosenbaum et al., 2011). In this study, emissions were defined as daily mass flows to given environmental compartments. The AV WWTP discharges its effluent to the ocean. The impact to both freshwater and ocean were evaluated for the importance of the choice of environmental compartments. No sludge from the AV WWTP is applied on land. Yet, in order to assess the impact of metals removed by the wastewater treatment process, the toxic impacts of the introduction of heavy metals to soil was assessed.

3. Results and discussion

Fig. 2 shows the comparison between measured concentrations of metals in influent (IN) and effluent (EF) and historical data from

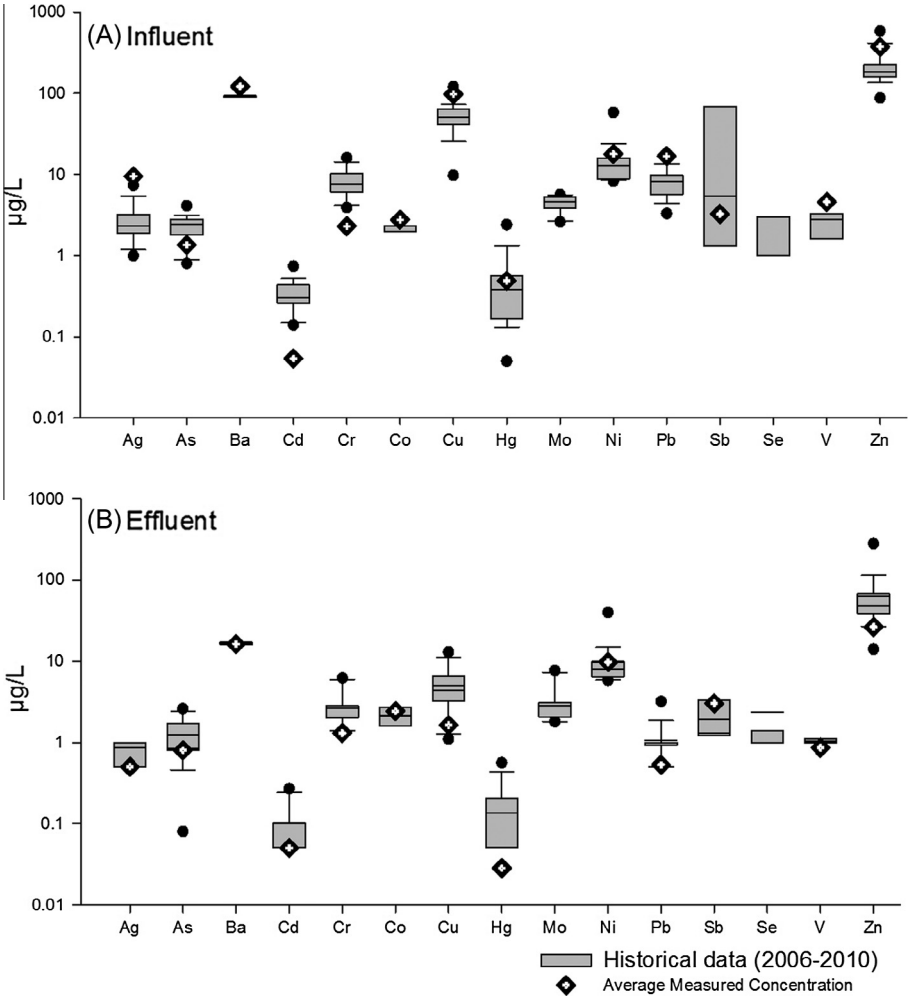

Fig. 2. Comparison of measured substance concentrations with historical data of Avedøre WWTP (A: influent and B: effluent). Box plots shows median, 10th, 25th, 75th and 90th percentiles as vertical boxes with error bars and maximum and minimum concentrations as black dots.

2006 to 2010. Analysis of influent and effluent qualities has been conducted routinely for selected metals at the AV WWTP. Measured concentrations generally agreed with the historical trend except for Cd and Hg. The average measured concentration of Cd in IN was about half of the average of the historical data. This could be explained by the steady decline in Cd concentration in IN over the years. The average influent concentration of Cd dropped from 0.46 µg L^{-1} in 2006 to 0.21 µg L^{-1} in 2010. As for Hg, the average measured concentration during the sampling campaign was below the detection limits of the routine assessment (0.05 µg L^{-1}).

Mass balances were successfully constructed for 24 out of the 32 elements analyzed in this study. Due to the limitation of the analytical methods, only partial mass balances were obtained for As, Br, Li, Mo, S, Se, Sn, and Sr. Fig. 3 shows the mass balance diagrams of TOC and P as examples of substance flows through the AV WWTP. Mass flow diagrams of other constituents are included in the Supporting material. The mass balance of wastewater and sludge flow showed reasonably good closure: out of 291 flows included in this assessment, 256 flows were accompanied by an uncertainty range smaller than 30%, and 160 flows by less than 10%. Flows calculated by subtraction, such as gaseous emissions and degradations, were accompanied by large uncertainty ranges, often above 100%.

3.1. Wastewater treatment process

During the sampling period, 60 000 t d^{-1} of wastewater, conveying 113 t d^{-1} of TS and 42 t d^{-1} of VS entered the AV WWTP on average. Twenty-six percent of TS and 53% of VS ended up in PS and SS, while 4.1% of TS and 12.6% of VS were degraded in the aeration basin. The fate of each constituent through the wastewater treatment processes is illustrated in Fig. 4(a). Thirty-seven substances were classified according to their fate and behavior. Biologically active elements, such as TOC, N, and LAS were subjected to microbial conversion and a significant portion of them were removed in the secondary treatment process: 20% of TOC, 68% of N, and 80% of LAS entering the AV WWTP. Elements such as Ca, Cl, K, Mg, and Na, which tend to form highly soluble salts, remained mainly in the treated effluent. Mn, Ni and Sb were equally divided between effluent and sludge. The remaining constituents appeared to have high affinity for solids and were largely removed by physical separation of solids and accumulated in sewage sludge. These findings are consistent with previous studies. Goldstone et al. (1990a,b,c) found that 71% of Ni in wastewater influent was dissolved whereas the corresponding numbers were 9% for Cu and 35% for Zn. Karvelas et al. (2003) reported similar results: 65–85% for Mn and 80–93% for Ni were reported to be in dissolved form and 75–95% of Cu, Cr, Pb, Cd and Zn were associated with particulate forms. Elevated concentrations of metals in sludge were found in this study, namely, 25-fold higher than the concentrations found in influent water.

The notable increase in Fe was due to the addition of ferric chloride sulfate (Kemira Pix-118) to enhance P removal. The increased Cl concentration in the effluent was less visible since the amount of Cl present in InAB was 10 times larger than Fe. Buzier et al. (2006)

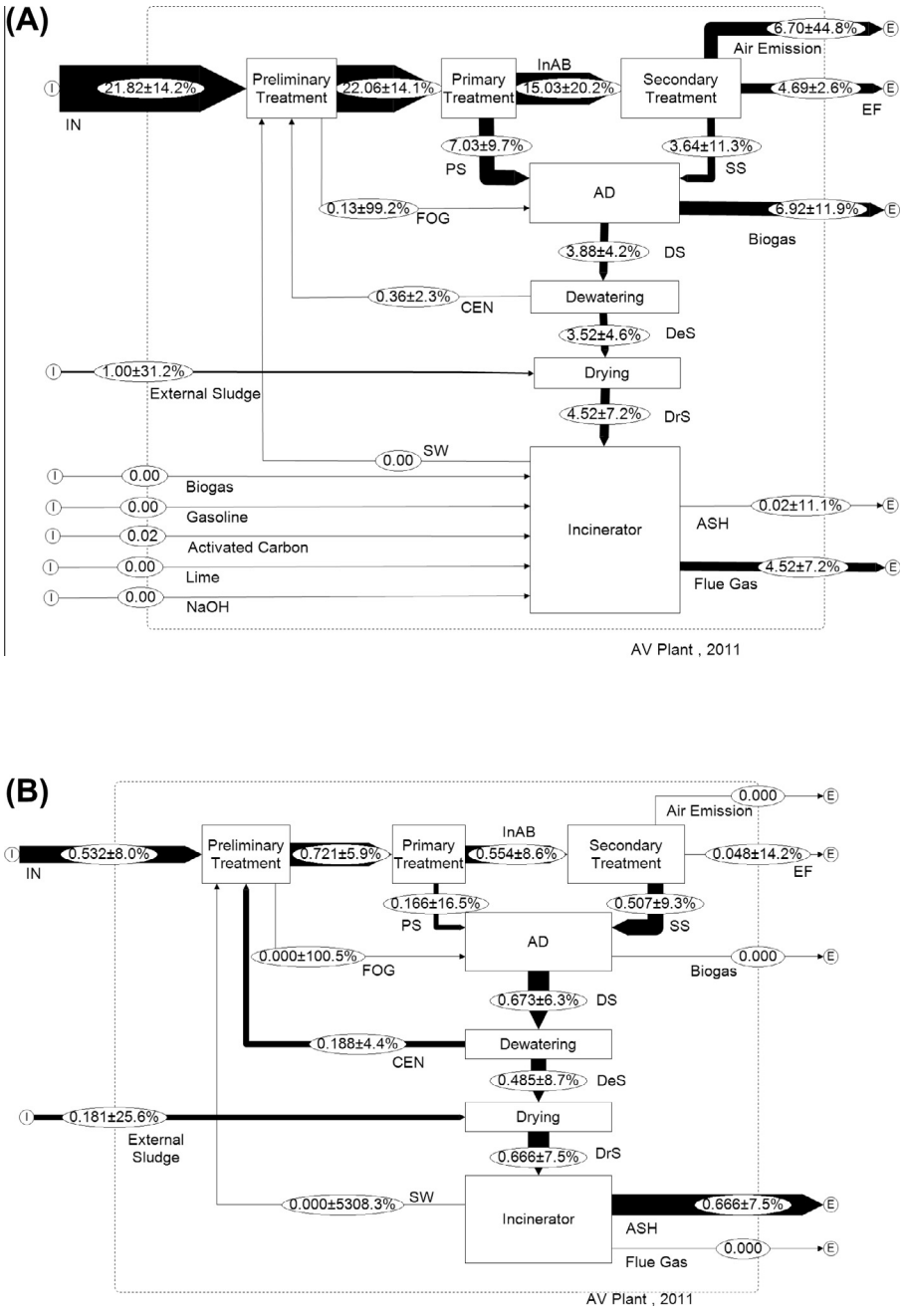

Fig. 3. Average daily substance flow of carbon (A) and phosphorus (B) through Avedøre WWTP in Mg d^{-1}.

pointed out that considerable amounts of Co, Cr, Cu, Ni, and Pb were found in the ferric chloride solution, contributing significantly to the metal concentrations in the effluent. However, no significant increase in these constituents in the effluent was observed in this study.

3.2. Sludge treatment process

During the sampling period, the AV WWTP produced 851 Mg of sludge on daily average, consisting of 46.3% PS, 53.0% SS and 0.67% FOG. PS and SS had TS contents of 4.23% and 2.70%, respectively, but after digestion the TS content dropped to 2.1%. Mechanical dewatering and thermal drying increased the TS content to 22.4% and 34.2%, respectively. At the end, 8.9 Mg of ash were produced and deposited in the landfill.

Fig. 4(b) presents the fate of each constituent through anaerobic digestion and dewatering. Due to the measurement and sampling uncertainty, the sum is not always equal to 100%. TOC, N, S, and organic pollutants were lost during the anaerobic digestion process. Forty-two percent of remaining TOC was converted to CH_4 and CO_2 and utilized for electricity and heat production. Twenty-two percent of S was most likely reduced to H_2S, and 13% of N was most likely subject to denitrification and ammonia evaporation. Samson and LeDuy (1982) observed a 16% loss of input N during anaerobic digestion.

Losses of Cl (42%), Hg (6%), and Sb (44%) during anaerobic digestion were also observed, though these numbers are associated with extremely high uncertainty ranges: 231% for Cl and 129% for Hg. Hg and Sb could be subject to bioconversion processes and transformed into methylated compounds under anaerobic conditions.

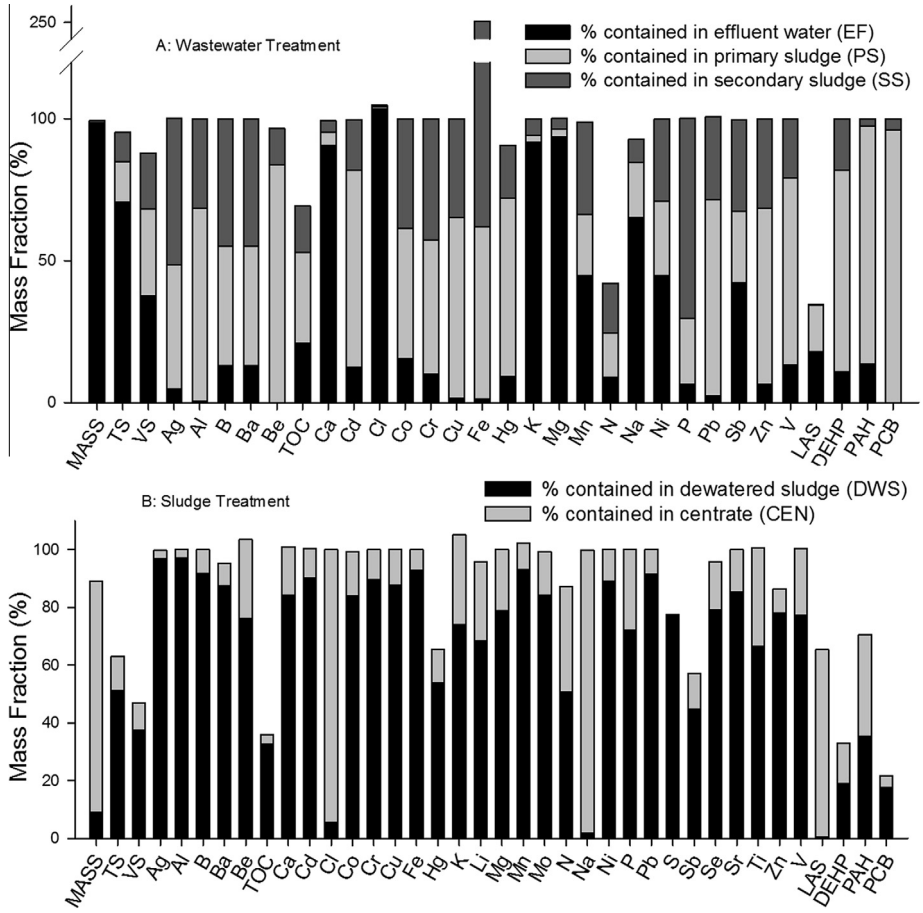

Fig. 4. Fate of substances in wastewater treatment (A) and sludge treatment (B).

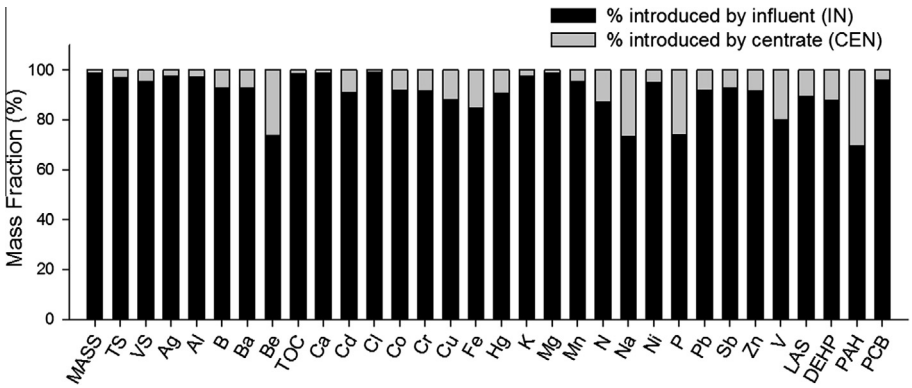

Fig. 5. Contribution of internal recycling to introduction of pollutants to wastewater treatment processes.

Two percent of input Hg and 0.1–0.8% of input Sb were reported to evaporate (Earle et al., 2000; Wehmeier and Feldmann, 2005; Gbondo-Tugbawa et al., 2010). Pilot scale operation of a municipal solid waste anaerobic digester reported 2–48% loss of Hg by volatilization (Earle et al., 2000). A previous mass balance study showed that up to 10% of Hg was unaccounted for in wastewater treatment plants (Balogh and Nollet, 2008). Methylated mercury and antimony are reported to be more mobile, bioavailable, and toxic than their non-methylated counterparts (ATSDR, 1999). Bioconversion of As, Sn and Se to volatile methylated hydride derivatives has been reported in landfills and biogas plants (Feldmann and Hirner, 1995). Further studies on the fate of these metals and their transport to the nearby ecosystem are anticipated.

The sludge dewatering process captured 98.2% of total solids and increased solid content by almost 10-fold. Cl and Na remained largely soluble and were removed by the dewatering process. Ca, K, Mg, Ni, and Sb exhibited a higher affinity for solids than PS and SS. Anaerobic digestion changes the oxidation state of elements, which affects their solubility: some metals are peptized by organic matter or occluded in its crystalline structure (Alvarez et al., 2002; Fuentes et al., 2004; Stasinakisa and Thomaidisb, 2010). The changes in metal and metalloid fractionation, together with degradation of

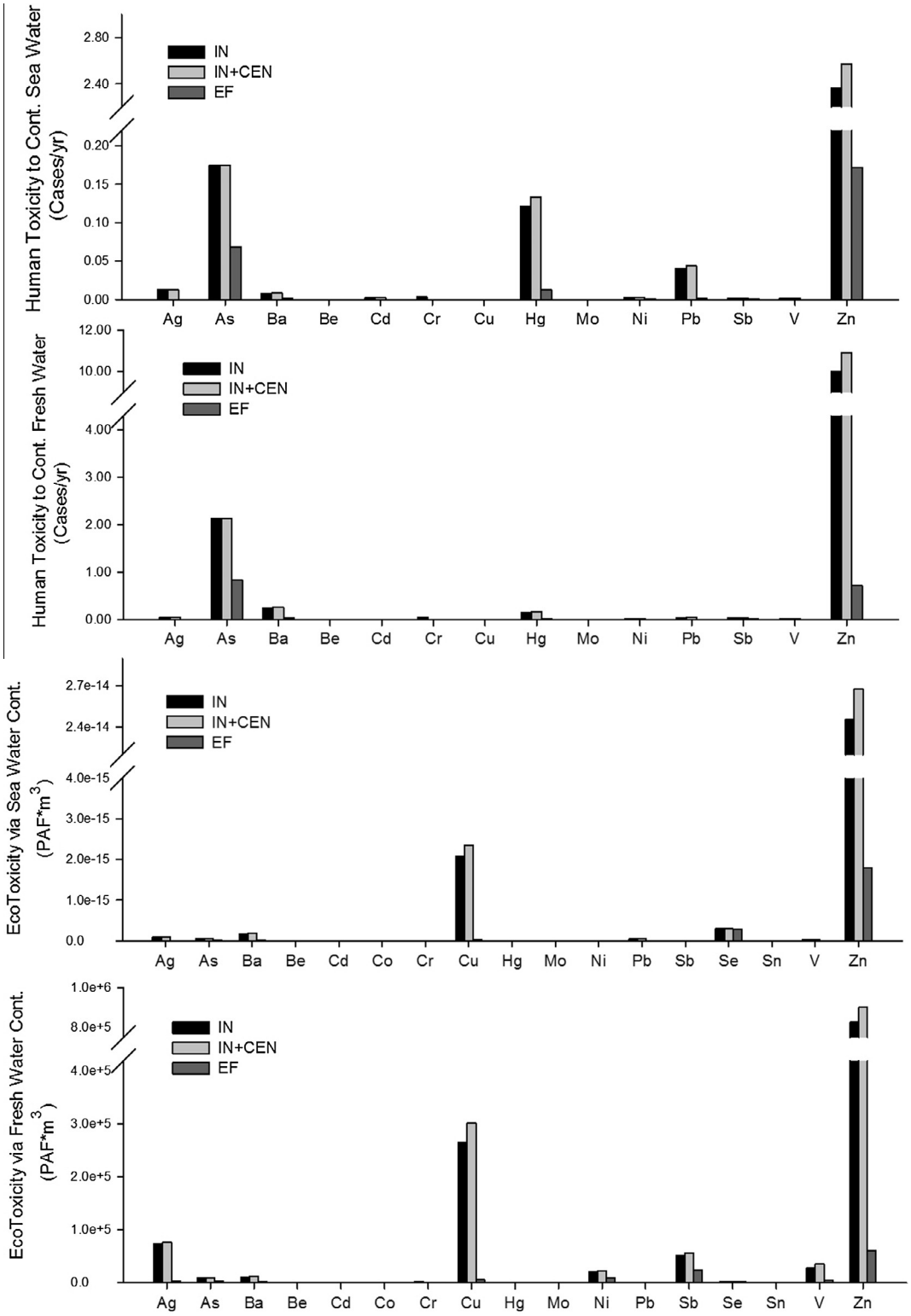

Fig. 6. Change in toxicity potential through wastewater water treatment. Comparison of influent (IN), influent with addition of centrate (IN + CEN), and effluent (EF). (A and B) Human toxicity introduced to sea water and fresh water, respectively. (C and D) Ecotoxicity introduced to sea water and fresh water, respectively.

volatile solids, contributed to elevated concentrations of metals in DWS.

Contrarily, the concentration of organic pollutants in sludge decreased through the anaerobic stabilization processes. Anaerobic dechlorination has proven effective at degrading even persistent organic pollutants, as documented in previous studies, e.g. 59–83% for PCBs (Benabdallah El-Hadj et al., 2007). The fraction of LAS degraded by the anaerobic digestion process was less than in the aeration process (33.8% vs. 77.9%), which is consistent with previous studies (Prats, 1997; Gejlsbjerg et al., 2003).

Incineration ash represented 0.015% of the total mass and 7.9% of the total solids in the influent. The concentrations of metals and metalloids were increased by 1000 to −10000 folds. PAHs and PCBs are reported to survive the incineration process (Dyke et al.,

2003); however, none of these organic pollutants were detected in the incinerated ash.

According to regular monitoring of flue gas constituents between 2006 and 2010, 0.13 g d^{-1} of Cd, 0.15 g d^{-1} of Hg, and 0.21 g d^{-1} of Pb were emitted with flue gas from the incinerator, representing 0.27%, 0.43% and 0.02% of the metals contained in ash. Balogh and Nollet (2008) studied an incinerator with a similar configuration of flue gas treatment as the one at AV WWTP and documented a loss of 2.1% of Hg in the flue gas emissions. Much higher values were reported by Van de Velden et al. (2008): 0.83% for Cd, 20% for Hg and 0.05% for Pb. The estimated stack emissions were at least 10 orders of magnitude lower than the uncertainty range associated with ash. This is one of the limitations of simple mass balance approach that minor flows such as stack emission, are masked by the uncertainty of major flows and would not be able to quantify precisely.

3.3. Side streams

Wastewater from the flue gas treatment process carried almost negligible amounts of elements back to the inlet, the highest being 0.023% for Cd and 0.0024% for Hg. This is much lower than previous studies which reported that 14.4–14.9% of Hg was partitioned into spent scrubber water and returned to the wastewater treatment process (Balogh and Nollet, 2008; Van de Velden et al., 2008). This is likely due to the injection of activated carbon before the bag filters, which absorbs Hg and other heavy metals. However, the relationship between the air pollution control technologies and fate of Hg are not clear. The Balogh and Nollet (2008) study reported similar levels of Hg in spent water from a facility equipped with activated carbon injection as for the facility without activated carbon studied by Van de Velden et al. (2008). This suggest that not only the configuration of air pollution control systems but also operational condition affect the fate of heavy metals in incinerators.

The internal recycling flow of centrate (CEN) equaled 1.1% of the flow entering the wastewater treatment stream, yet was found to contain significant portions of the constituents' mass flows. As shown in Fig. 5, more than 20% of Be, Na, P, V and PAH in the wastewater treatment streams originated from CEN. Though evidence is limited, the internal recycling of reject water from the sludge treatment process might improve the removal efficiencies of certain metals through the introduction of additional suspended solids and coagulants (Goldstone et al., 1990; Buzier et al. 2006).

However, it is also true that the internal recycling flow of centrate burdens the removal of pollutants through the wastewater treatment process. As much as 25% of P entering the wastewater treatment process was introduced through the internal recycling flow. The P accumulated in bacterial biomass is released as phosphate ions when the phosphate-laden cell biomass is exposed to oxygen-deprived conditions. It is believed that Al-, Ca-, and Fe-bound P are not released during the anaerobic digestion process, though there is some evidence that the conditions in the digester (e.g. reduced pH and low redox conditions) favor the release of phosphate (Yeoman et al., 1988). Indeed, P fractionates to smaller particulate sizes that are not captured by the mechanical dewatering process (Greaves et al., 1999). The concentration of P in the side stream was 27.1 times higher than in the wastewater influent, which supports reported attempts to target side streams for purposeful removal and recovery of P through chemical precipitation and adsorption (Münch and Barr, 2001; Shu et al., 2006; Ivanov et al., 2009).

3.4. Toxicity characterization

The USEtox impact assessment method covers 15 inorganic pollutants for human toxicity and 16 for eco-toxicity (Rosenbaum et al., 2011). It provides characterization factors expressed for human toxicity as number of disease cases per kg of substance emitted to certain environmental compartments (cases kg^{-1}) and, for ecotoxicity, as the potentially affected fraction of species (PAF) integrated over time and volume per unit mass of a chemical emitted (PAF m^3 d kg^{-1}). Thallium was excluded from this characterization step since its concentration was below the detection limit. It has been well documented that the speciation of the metal and metalloids determine its toxicity, but at the time this article was written, USEtox provided a characterization with metal speciation only for Cr ((III) and (VI)). Previous studies found that Cr in treated wastewater is in trivalent form (Jan and Young, 1978; Tu et al., 2012). In this study, it was assumed that 98% of Cr is present in Cr (III) and the rest in more toxic Cr (VI) form.

Fig. 6 shows changes in toxicity potentials through the wastewater treatment plant. Two scenarios are presented: the discharge to sea water as well as to freshwater. The removal of inorganic pollutants reduced toxicity potentials in the two scenarios: a reduction in human toxicity by 90.5% was observed in the seawater scenario and by 87.0% for freshwater, while the ecotoxicity decreased by 91.2% (sea water scenario) and 92.4% (freshwater scenario). In all four cases, Zn appeared to be the substance of concern, contributing 43.8–89.9% of the total toxic potential of the wastewater effluent. The dominance of Zn in impact categories has been reported by previous studies using USEtox for toxicity assessment: Gandhi et al. (2011) reported that up to 98% of freshwater eco-toxicity is from the emission of Zn to water. Gandhi et al. (2011) cites a large uncertainty range associated with the characterization factor but other means of risk assessment such as metal speciation or fate modeling in the environment also suggest that Zn could potentially be the element of concern due to its high concentration, mobility, and bioavailability (Tu et al., 2012; Spildevandscenter Avedøre, 2013).

All stabilized sludge is currently incinerated and not applied on agricultural land. However, the concentrations of the 7 heavy metals (Cd, Cr, Cu, Hg, Ni, Pb, and Zn) included in the Danish regulation were under the limit values, thus, the sludge could be applied on land. Toxic impact potentials associated with the disposal of sludge on land are shown in Fig. 6. Zn, again, appeared to contribute the largest share of toxic impact potential (89.7% for human toxicity through contamination of agricultural soil and 53.2% for eco-toxicity via agricultural soil). The 7 metals currently regulated represent 97.2% of human toxicity and 89.3% of eco-toxicity via agricultural soil when the 15 inorganic elements characterized in USEtox are included.

4. Conclusion

Comprehensive substance flow analyses of a conventional wastewater treatment plant were conducted. The results show that the mass balance approach can be applied to determine the fate of constituents in the main individual treatment processes within the wastewater treatment plant as well as the overall removal rates. However, direct measurements are necessary for gaseous emissions due to the large uncertainties associated with mass flows. The study showed that internal return flows, e.g. from sludge centrifugation, despite low volume, could be significant in terms of substance mass; for P and Be they constituted as much as a quarter of the mass flow. Since return flows represent less than 1% of the influent water entering the wastewater treatment plant, reduction of the pollutant load in the internal recycling flow could contribute to improving the overall performance of wastewater treatment plants.

The fates of a total of 33 substances were reported. Although specific characterization factors are not available for all these

substances, it is not expected that including these would significantly change the toxicity level of the wastewater or the reduction in toxicity observed for the wastewater treatment plant. Zn appeared to be the most crucial element in the toxicity impact assessment of the treated wastewater discharge to the environment and utilization of stabilized sewage sludge on land.

The study confirmed that wastewater treatment plants are effective in removing not only conventional heavy metals, but also other metals, metalloids and organic pollutants, and reducing potential toxic impacts to receiving waters and public health.

Acknowledgement

The authors thank 3R (Residual Resource Research) Institute at the Technical University of Denmark for providing PhD scholarship to carry out the sampling campaign.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.09.045.

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