

Ten-years monitoring of MSWI bottom ashes with focus on TOC development and leaching behaviour

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In Switzerland MSWI bottom ash has to comply with the legal threshold value for TOC of <2 wt.-% in order to be landfilled. However, TOC contents of this magnitude lead to elevated DOC emissions and associated emissions of ammonium and Cu (aq). Since 2008 the Canton of Zürich therefore pursues a strategy to lower TOC contents in bottom ash by 2020 to 0.5 wt.-%. To observe the development of TOC and other constituents, bottom ash has been monitored from 2008–2018. Monitoring results indicate that TOC contents <0.5 wt.-% in bottom ash lead to DOC eluate concentrations <20 mg/l. DOC concentrations of this magnitude are close to Swiss legal criteria for discharge of landfill leachate into surface waters (10 mg/l). The emission results have been obtained by batch eluate tests according to Swiss Waste Legislation. Such laboratory tests only partially simulate real conditions occurring on landfills. To approximate landfill conditions, column tests with recent bottom ashes combined with tests on simple emission forecasting complete the study. The comparison of results from batch and column tests shows similar cumulative concentrations, indicating that batch tests are suitable to evaluate bottom ash quality. The tested modelling ap-

proach, based on constant conditions and exponential decrease in concentration, proved adequate to simulate column progressions. The modelled emission forecasts for DOC lies within 33% of column test results. Further, the model demonstrates the differences in flow regime between eluate tests and landfills and promotes better understanding of temporal aspects and the influence of landfill relevant parameters on pollutant mobilisation.

Keywords: Municipal solid waste incineration, bottom ash, TOC, monitoring, leaching tests, emission forecast

1 Introduction

Switzerland has a long tradition of sustainable waste management based on the Swiss Environmental Protection Law (Swiss Confederation, 1983) and specified by the Guidelines for Waste Management in 1986 (Federal Office for the Environment, 1986). These guidelines propose that only two types of material should be produced in waste management: (1) recyclable materials and (2) residual materials suitable for storage in final repositories. These strict requirements resulted in the prohibition to landfill unburnt municipal solid waste in the year 2000. At present, 4 million t/y of non-recyclable waste are incinerated in 30 municipal solid waste incineration (MSWI) plants in Switzerland (Federal Office for the Environment, 2017a). Main objectives of thermal waste treatment are mass and volume reduction, destruction of organic compounds, energy and metal recovery and transformation of the remaining fraction into inert incineration residues. About 20 wt.-% (750'000 t/y) remain as bottom ash, which consists mainly of non-combustible materials and residual amounts of unburnt organic matter.

Bottom ash is composed of Si- and Ca-dominated crystalline and amorphous compounds (~85 wt.-%), followed by ferrous (~9 wt.-%) and non-ferrous metals (~3.5 wt.-%) and carbon constituents (~2 wt.-%) (Ferrari et al., 2002; Eggenberger and Mäder, 2010; Bunge, 2014). Total carbon (TC) is composed of total inorganic carbon (TIC) and total organic carbon (TOC). TIC comprises mainly of carbonate carbon whereas TOC is bound to organic matter, which has not been oxidised during incineration. Only a fraction of TOC consists of degradable organic carbon (OC) which is readily soluble and relevant for mobilisation of dissolved organic carbon (DOC) via landfill leachate (Ferrari, 1997; van Zomeren and Comans, 2009). The residual elemental carbon (EC), however, has no leaching potential. Generally, the composition of landfill leachates at early stages is controlled by the dissolution of Ca containing bottom ash phases, playing a major role in buffering the system (Johnson et al., 1999). Under the

resulting alkaline conditions, the mobility of heavy metals is limited and controlled primarily by sorption and complexation. For the latter, organic ligands are of importance as is well known for copper (Cu) with a strong affinity for DOC. The correlation between these two species has been determined in many studies (Comans et al., 1993; Johnson et al., 1996; Chandler et al., 1997; van Zomeren and Comans, 2004; Dijkstra et al., 2006). Beside DOC, the ecotoxic ammonium (NH_4^+) is another organic constituent in bottom ash that is leached in high concentrations, independent on pH conditions (Mayerhofer, 2017).

In order to limit the organic load in landfill leachates the Swiss Environmental Protection Law demands minimisation of TOC. This has been specified by the Swiss Waste Ordinance (Swiss Confederation, 1990; Swiss Confederation, 2016) by defining a threshold value for TOC of <3 wt.-% in 1990 and lowered to <2 wt.-% in 2016. Since the national requirements are minimum requirements, it is up to each cantonal authority to define its own stricter guidelines. The environmental authority of the Canton of Zürich (Office for Waste, Water, Energy and Air - AWEL) observed that the threshold value for TOC still leads to high emissions of DOC. Thus, together with the six cantonal MSWI plants a target value for TOC concentration in bottom ash has been defined in 2008. The target value aims at a TOC concentration in bottom ash of 0.5 wt.-% to be reached by 2020 (AWEL, 2011). It has been shown that this TOC value should ensure DOC concentrations in leachates of <20 mg/l (Morf, 2009; Kuhn and Morf, 2010; Morf and Kuhn, 2010; AWEL, 2019). This lies in the range of the threshold value for discharge of landfill leachate into surface waters (10 mg DOC/l) according to the Swiss Water Protection Act (Swiss Confederation, 1998). To comply with the defined goals for TOC, burn-out of the waste must be optimised at each MSWI plant. The content of TOC is controlled by numerous factors like incineration temperature and time, dimension of the furnace, primary air preheating, plant and discharge technology and waste throughput (Koralewska, 2019).

The aim of this study is to investigate the environmental impact of reducing TOC content in bottom ash due to the introduction of the target value for TOC of 0.5 wt.-%. For this, a ten-year monitoring period (2008–2018) of the six MSWI plants in the Canton of Zürich (Plant A–F) has been conducted of which selected results are presented. The focus of the study is laid on the role of TOC as a controlling factor for landfill emissions with special regard to the relation of DOC, Cu (aq) and NH_4^+ . For this reason, the leaching behaviour of each bottom ash sample at specific conditions is determined based on batch tests according to the Swiss Waste Ordinance. However, the conditions applied in these batch eluate tests hardly depict conditions as they occur in a landfill. There, an increasing liquid to solid ratio (L/S) with time and preferential flow paths lead to a heterogeneous leaching. To classify and interpret the results from the batch tests of the monitoring, up-flow column tests with recent bottom ashes complete the study. Data from these column tests is subsequently used to evaluate the suitability of a common model for simple emission forecasting. The detailed investigation of TOC and its correlation with DOC, Cu (aq) and NH_4^+ contributes to a better understanding of the leaching processes of these environmental harmful substances and points out the importance of these parameters concerning the duration of aftercare for bottom ash landfills. The results of this study allow improving of bottom ash quality towards lower emissions and shorter aftercare.

2 Materials and methods

2.1 Monitored MSWI plants

The technical details of the six monitored MSWI plants in the Canton of Zürich are shown in Table 1. In average, waste input consists of 48 wt.-% municipal and 44 wt.-% industrial solid waste, 7.4 wt.-% hazardous waste and 0.5 wt.-% sewage sludge with an average calorific value of 12.2 MJ/kg. All plants operate with grate furnace systems with incineration temperatures of 700–960°C. The majority of the plants have adjustable primary air preheating up to 160°C, which supports high burnout quality (Koralewska, 2019). Regarding the bottom ash discharge system over the monitoring period, significant differences are recognisable. From 2008–2015 five plants (Plant B, C, D, E, F) used wet discharge, where the bottom ash is falling from the end of the moving grate into a water bath. The water in the discharger ensures that flue gas is separated from atmospheric air, while a discharging ram forces the bottom ash over the drop-off edge draining excess water by the compressing action. The three furnace lines in Plant A have been modified for dry discharge stepwise from 2007–2016, while Plant B and E changed from wet to dry discharge in 2016. Performing dry discharge, the bottom ash is discharged onto a vibrating conveyor, where it is air-cooled by injected tertiary air. The main objective of this technology is to enhance the rate and quality of recovered metals, by preventing metal corrosion and caking of ash particles on the metal surfaces as well as an improved burnout quality (Böni and Morf, 2018).

Table 1: Technical details and applied changes of investigated MSWI plants during the monitoring time.

Parameter	Plant A	Plant B	Plant C	Plant D	Plant E	Plant F
Type of furnace	grate furnace	grate furnace	grate furnace	grate furnace	grate furnace	grate furnace
Line	3	2	2	2	1	1
Load	1 x 40 MW 2 x 22 MW	2 x 48 MW	2 x 18 MW	1 x 38 MW 1 x 48 MW	1 x 15 MW	1 x 48 MW
Throughput	1 x 11.4 t/h 2 x 6.3 t/h	2 x 14.4 t/h	2 x 10 t/h	1 x 10.5 t/h 1 x 12.5 t/h	1 x 4.2 t/h	1 x 14.7 t/h
Designed lower heating value (MWh/t)	3.5	3.4	3.5	3.6 / 3.9	3.6	3.3
Mean lower heating value 2015-17 (MWh/t)	3.4	3.4	3.5	3.3	3.5	2.9
Air preheating	max. 160°C	max. 140°C	max. 160°C	max. 100°C	max. 160°C	130°C
Incineration temperature	800/780/810°C	900/860°C	900/900°C	930/870°C	700°C	960°C
Discharge technology	dry (stepwise since 2007)	dry (since 2016)	wet	wet	dry (since 2016)	wet
Produced bottom ash (t dry/year)	35'600	36'100	16'400	38'960	5'100	26'160

Four other Swiss MSWI plants situated outside the Canton of Zürich operating with wet discharge and producing 10'000 – 50'000 t bottom ash per year supplement this study. Data from these plants served to model an emission forecast for DOC concentration.

2.2 Sampling and sample preparation

From 2008–2018 sampling campaigns were performed on a regular basis at all six MSWI plants with the identical sampling procedure. During selected months, samples of ~12 kg of untreated bottom ash (mixture of all furnace lines) were collected daily on the conveyor belt after wet or dry discharge. The increments, stored in an air-tight container, have been homogenised (monthly composite sample) and split into two representative samples of ~12 kg at the end of the month. One composite-sample was retained, the other split in two parts, which were used for (1) solid chemical analysis and (2) batch eluate tests. The preparation of the material for these two purposes was performed differently: (1) the material was dried at 105°C and subsequently crushed to a grain size <1 mm, while metals and unburnt material were manually separated. In an additional step the material was milled to <0.1 mm. (2) the

material was sieved at 5 mm in its original condition, while particles >5mm were crushed and subsequently mixed with the material portion <5mm.

Bottom ash used to perform column tests derives from four Swiss MSWI plants outside the monitoring of the Canton of Zürich. These plants operate with wet discharge and the sampling was performed similarly in 2015. The material was subsequently crushed in its original condition to a grain size <5 mm, while metals and unburnt material were manually separated.

2.3 Chemical analysis

The bottom ash samples were analysed based on the criteria of the Swiss Waste Ordinance according to certified procedures (Bachema AG, 2017). The most relevant parameter TOC was monitored during the entire period, however, other C-constituents, N, Cu and the eluate composition was only measured in the period 2008–2015 and OC from 2011–2013.

2.3.1 Chemical composition

Test portions of 0.5 g bottom ash <0.1 mm were digested with a mixture of 3 ml hydrochloric acid, 8 ml nitric acid and 3 ml hydrofluoric acid. Free hydrofluoric acid was bound with boric acid and the mixture subsequently heated in three steps to 175°C using a high-pressure microwave system. In this total digest Cu was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (ISO 11885, 2007). Total contents of C and N were determined using a EuroEA CHNS-analyser (EN 15936, 2012). The composition of C was additionally characterised by TOC and TIC with the same method as used for TC. Finally, applying another method based on temperature-dependent combustion of carbon (DIN 19539, 2016) using a Primacs SCN-100 analyser, the differentiation of TOC into degradable organic carbon (TOC400 or OC) and residual oxidisable carbon or elemental carbon (ROC or EC) was achieved. The TIC900, which is released from 400 to 900°C is the third fraction produced with this method and corresponds to the TIC.

2.3.2 Leaching behaviour

Batch tests have been performed with a liquid to solid (L/S) ratio of 10 during 24 h according to the Swiss Waste Legislation (Federal Office for the Environment, 2017b). Further, Swiss Waste Legislation demands CO₂-saturated water for the elution of cationic heavy metals simulating acid rain conditions. For this reason, batch tests have to be performed in two parts: Test 1 - Mixing of bottom ash in its original condition with CO₂-saturated water for the determination of Cu (aq). Test 2 - Mixing of bottom ash in its original condition with neutral water for the determination of DOC and NH₄⁺. Saturation with CO₂ is achieved by continuous injection of ~50 mL CO₂/min through a glass tube into the elution vessel. Although Swiss Waste Legislation defines the threshold value for Cu (aq) by Test 1, concentrations from the same test (Test 2) were used to compare DOC and Cu (aq) this study. To distinguish the Cu results obtained from the two different tests, Cu analysed in Test 1 is referred to as Cu (aq + CO₂), while Cu (aq) is used for results from Test 2.

Column tests were performed according to European standard (CEN/TS 14405, 2017), where bottom ash is packed 30 ±5 cm high into a glass column with 5 cm diameter and leached with neutral water using up-flow-percolation with a flowrate of 12 ml/h. At specified L/S ratios (0.1, 0.2, 0.5, 1, 2, 5, 10) the eluates were sampled and DOC analysed. The analyses of Cu (aq) was performed by inductively coupled plasma mass spectroscopy (ICP-MS) (EN ISO 17294-2, 2016), DOC was determined by thermal oxidation (EN 1484, 1997), NH₄⁺ photometric with an Aquakem-System (DIN 38406-5, 1983).

2.3.3 Outliers

Due to the size of the dataset and the heterogeneity of the sampled bottom ash, inconsistency in material handling and analytical uncertainties cannot be excluded. Because of this, all values undercutting the lower quartile or exceeding the upper quartile by more than 1.5 times the interquartile range (IQR) in boxplots are considered outliers (Tukey, 1977).

2.4 Modelling

The column tests carried out were supplemented by modelling according to Lauer et al. (2011), a model commonly used for simple risk assessments of landfilled material in Switzerland, but not specifically for bottom ash. The modelling approach is based on constant landfill conditions and exponential decrease of the pollutant concentration in the leachate. The strength of this model lies in the temporal classification of the collected fractions of the column test. The modelled concentration development was compared to measured column test data in order to estimate the suitability of the model to predict emissions from bottom ash landfills. The model calculates the concentration of a constituent at time t ($c_a(t)$; mg/l) based on equation (1):

$$c_a(t) = c_0 \times e^{-\left(\frac{c_0}{m_v} \times \Delta \frac{L}{S} \times h\right) \times t} + c_{org} \times e^{-\left(\frac{c_{org}}{m_{org}} \times \Delta \frac{L}{S} \times h\right) \times t} \quad (1)$$

- c_0 = initial concentration of readily soluble material at the end of deposition (mg/l)
- c_{org} = initial concentration of persistent organic material at the end of deposition (mg/l)
- m_v = total mobilisable fraction (mg/kg)
- m_{org} = emission potential of persistent organic material (mg/kg)
- $\Delta L/S$ = annual change of L/S (l/kg*a)
- h = heterogeneity factor of water flow in the landfill (-)
- t = time after end of deposition (a)

The model is adopted for DOC by considering both readily soluble shares and persistent shares with retarded availability due to biochemical processes. For the readily soluble share, the parameters c_0 and m_v have been determined experimentally with column tests. For the persistent organic material the parameters c_{org} and m_{org} are estimated based on measured OC/TOC ratios. $\Delta L/S$ originates from averaged measurements from Swiss bottom ash landfills. Finally, the heterogeneity factor (h) is varied to model a scenario corresponding to the performed column test and another scenario where conditions on a landfill are approximated.

3 Results

3.1 Bottom ash monitoring

The average concentration of TC in bottom ash from all MSWI plants is 1.4 wt.-% within a range of 0.6 to 2.4 wt.-% (Table 2). Approximately 60 % of the TC account for TOC with a correlation of 0.76 in the period from 2008–2015 (Figure 1a). The average concentration of TOC is 0.7 wt.-% (0.03–1.6 wt.-%), whereas 82 % of the samples have a TOC concentration <1 wt.-% and 25 % <0.5 wt.-%.

Table 2: Concentration of specific constituents and pH of batch eluate Test 1 and Test 2 of bottom ashes from Plant A–F over the monitoring period (2008–2018). Number of measurements (N), average ($\bar{\phi}$), median, minimum, maximum concentration and number of outliers ($\downarrow = <1.5*IQR$, $\uparrow = >1.5*IQR$).

	Parameter	Unit	N	$\bar{\phi}$ *	Median	Min.	Max.	Outliers ($</>1.5*IQR$)
C-constituents	TC	wt.-%	117	1.4	1.5	0.6	2.4	1 \uparrow
	TIC	wt.-%	112	0.6	0.6	0.05	1.1	1 \downarrow
	TOC	wt.-%	160	0.7	0.8	0.03	1.6	1 \uparrow
	OC	wt.-%	40	0.3	0.2	0.04	0.7	-
	EC	wt.-%	40	0.5	0.5	0.2	0.9	-
	DOC	mg/l	115	32	24	2.7	100	-
N	N	wt.-%	118	0.05	0.03	0.01	0.8	7 \uparrow
	NH ₄ ⁺	mg/l	116	3.01	2.44	0.03	11.57	4 \uparrow
Cu	Cu	mg/kg	118	5'995	5'800	1'810	13'400	3 \uparrow
	Cu (aq + CO ₂)	mg/l	115	0.71	0.73	0.002	1.97	-
	Cu (aq)	mg/l	53	1.04	0.86	0.11	4.32	1 \uparrow
pH	Test 1 (CO ₂ sat.)	-	111	6.9	6.9	6.4	8.2	1 \uparrow
	Test 2 (neutral)	-	112	12.4	12.4	11.8	13.1	5 \uparrow / 4 \downarrow

* refer to supplementary data article in Data in Brief for fully tabulated results.

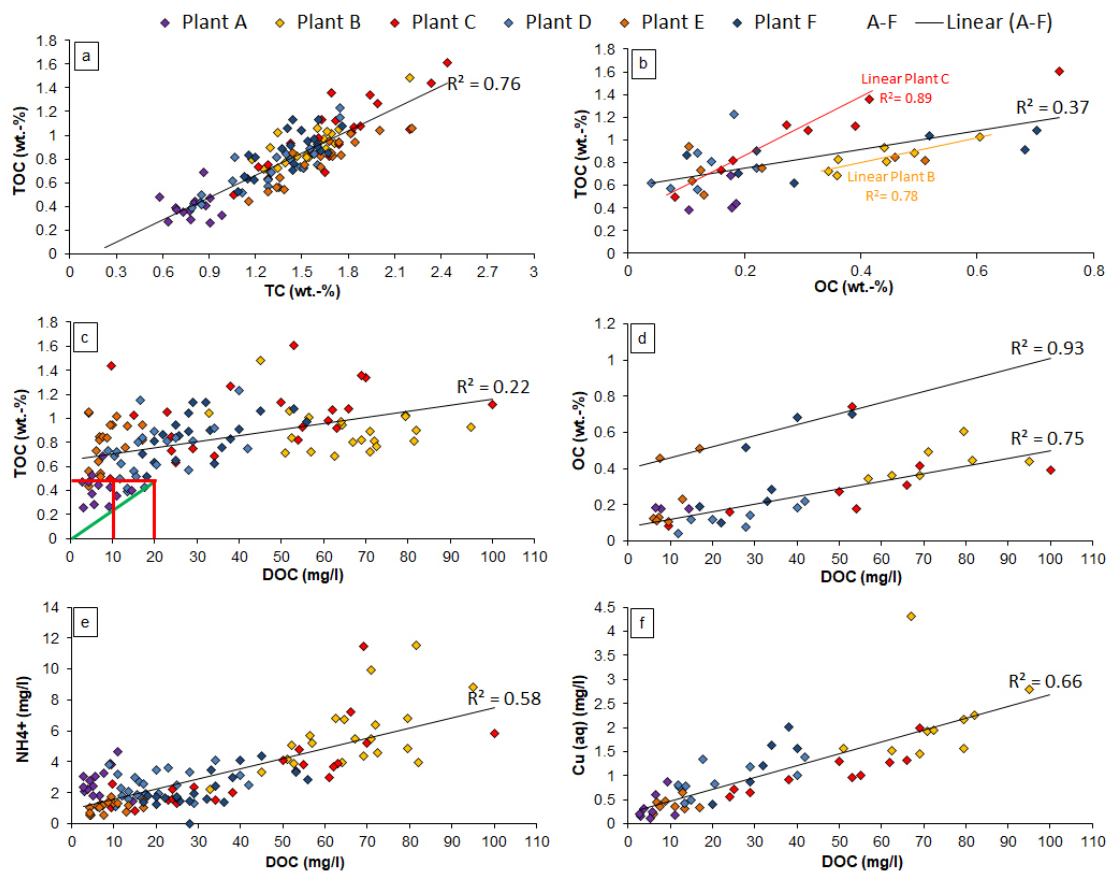


Figure 1: Correlations of concentrations in bottom ash between (a) TOC and TC, (b) TOC and OC, (c) TOC and DOC, (d) OC and DOC, (e) NH_4^+ and DOC and (f) Cu (aq) and DOC during the monitored period from 2008–2015.

TOC concentration of bottom ash from all plants shows temporal variation from 2008–2018 (Figure 2a). The most pronounced variation is observed in Plant C, where the TOC concentration follows a seasonal trend with high values (>1 wt.-%) in winter and low values (<1 wt.-%) in summer. A slight linear downward trend for TOC concentration is observed from 2008–2018 for Plant C. For all other plants, the annual fluctuation is less distinct and the intervals between high and low values are not correlated to seasonal changes. All plants, except Plant F, show an overall linear downward trend over time for TOC concentration with an average decreasing trend from 1–0.5 wt.-% within the monitoring period 2008–2018.

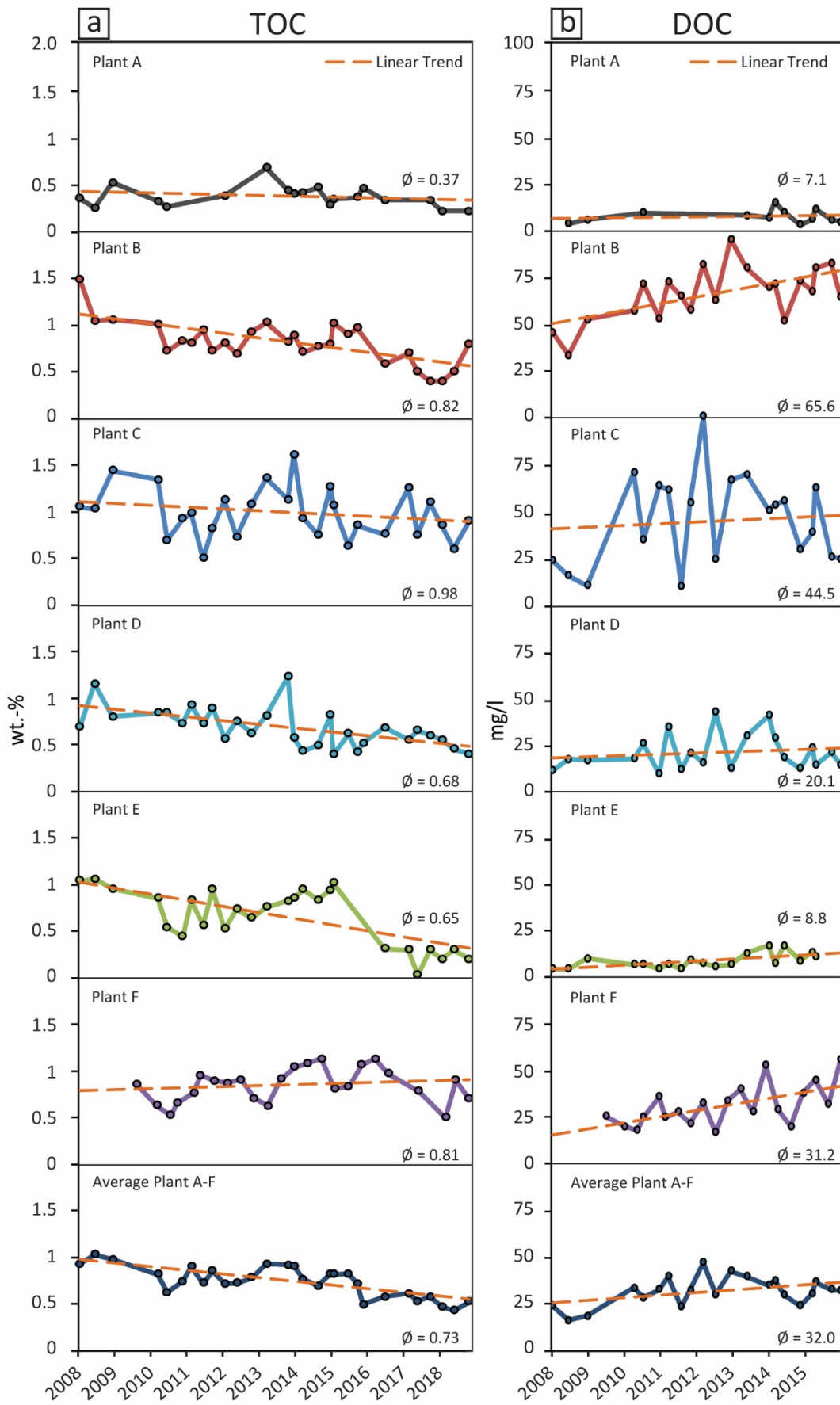


Figure 2: Temporal evolution of (a) TOC concentrations in bottom ash and (b) DOC concentrations in eluates from batch tests for the monitored Plants A–F.

Looking at the composition of the TOC species, it is composed on average of 0.3 wt.-% degradable OC (0.04-0.7 wt.-%) and 0.5 wt.-% EC (Table 2). Bottom ash from Plant B ($R^2 = 0.78$) and C ($R^2 = 0.89$) show a good correlation for TOC and OC, while the overall correlation is low ($R^2 = 0.37$) (Figure 1b).

The OC concentration in bottom ash for Plant A, B and D remains stable between 2011 and 2013 (Figure 3), showing low average concentrations of ~0.15 wt.-% for Plant A and D and high average concentrations of ~0.40 wt.-% for Plant F. Consequently, Plant D shows the lowest OC/TOC ratio (0.16) and Plant B the highest (0.49). The OC/TOC in Plant A is 0.34, as not only OC but also TOC shows low concentrations compared to the overall average. In Plant C and E OC concentrations in bottom ash vary by a factor four, in Plant F even by a factor six from 2011–2013.

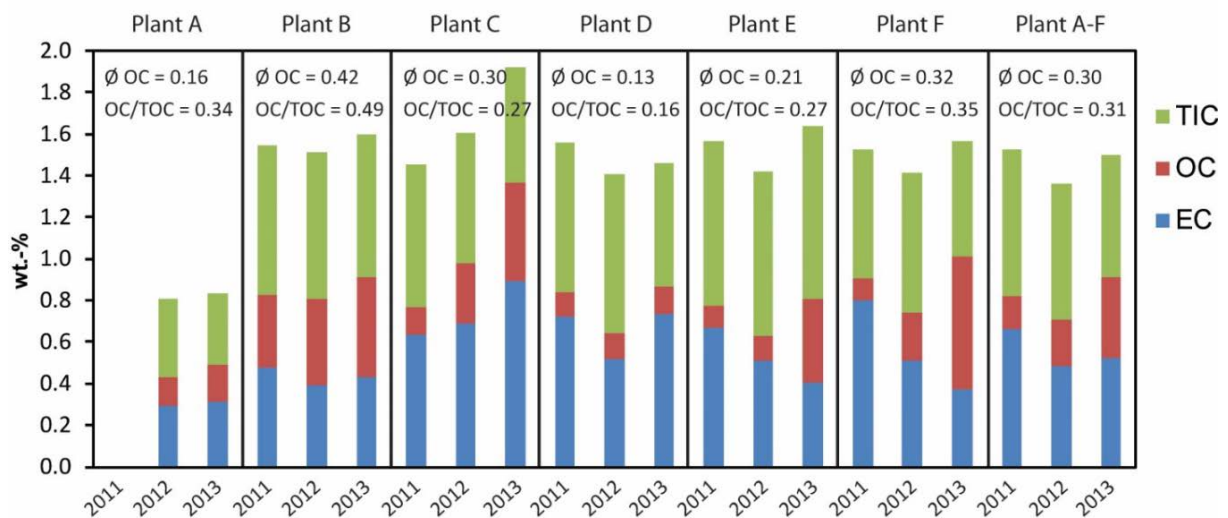


Figure 3: Proportions of TIC (green), EC (blue) and OC (red) in bottom ash per plant for the period from 2011–2013.

Batch tests according to the Swiss Waste Ordinance (24 h at L/S 10) result in a conductivity of the eluate of 8'400 $\mu\text{S}/\text{cm}$ on average, a pH value of 12.4 for the pure water test and a pH value of 6.9 for CO_2 -saturated water extraction (Table 2). The average DOC concentration in the eluates is 32 mg/l, ranging from 3–100 mg/l (Figure 2b). Plant A and E show the most stable and lowest average DOC concentrations (<10 mg/l), with values 2–6 times lower than of the other plants. On the other hand, eluates of Plant B and F trend towards increasing DOC

concentrations from 50 to 80 mg/l and 20 to 40 mg/l, respectively over the years. No trend for DOC concentration is observed for Plant C and Plant D where the concentrations fluctuate strongly over the monitored period.

Beside TOC, nitrogen-containing organic substances remain in bottom ash, of which especially NH_4^+ poses a risk to the environment. The average concentration of nitrogen in bottom ash is 0.05 wt.-%, resulting in an average NH_4^+ concentration in the pure water eluate test of 3 mg/l (Table 2). The closer look at the heavy metals shows, that Cu is present in bottom ash in a concentration of ~6'000 mg/kg on average, resulting in an average Cu (aq) concentration of 1.04 mg/l. In the CO_2 -saturated eluate test, which is relevant for the determination of heavy metals according to Swiss Waste Legislation, the average Cu (aq + CO_2) concentration is 0.71 mg/l.

3.2 Column tests and modelling

The results of the bottom ash monitoring show that TOC concentrations <0.5 wt.-% lead to DOC concentrations <20 mg/l in batch eluates performed at L/S 10 (Figure 1c). In order to assess the reliability of this correlation, data from batch tests are compared to the average concentration development from column tests. These column tests were performed with bottom ash from four Swiss MSWI plants, outside the monitoring of the Canton of Zürich, operating with wet discharge. The high concentration of DOC (256 mg/l) in the initial fraction of the column test (L/S 0.1) decreases rapidly with increasing L/S so that up to L/S 5, 80 % of TOC is mobilised as DOC (Figure 4a). The cumulative DOC concentration at the end of the experiment (L/S 10) is 28 mg DOC/l (Figure 4b). Thus, it lies in the same range as the average DOC concentration of the batch tests from the bottom ash monitoring of the Canton of Zürich (32 mg DOC/l).

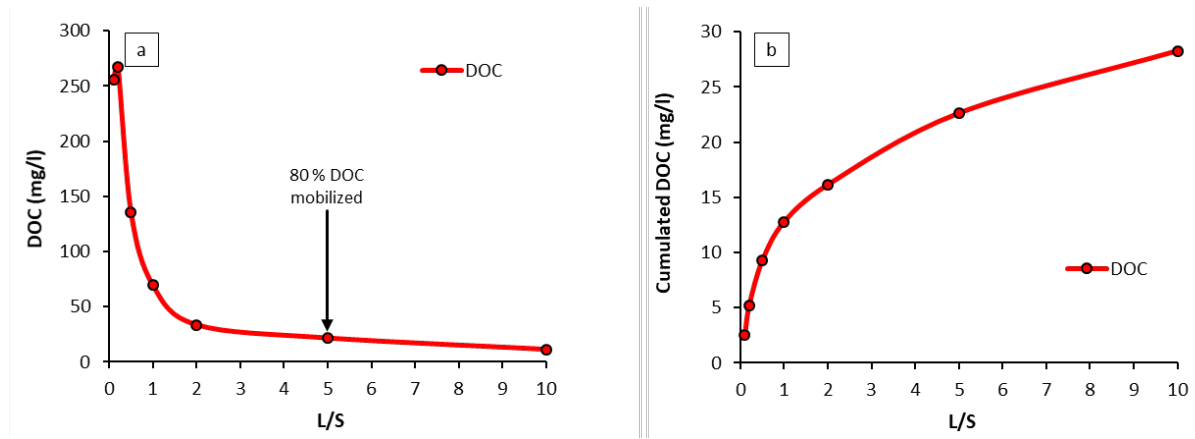


Figure 4: (a) Average DOC concentrations at specified L/S ratios measured in column tests performed with bottom ash from four MSWI plants outside the monitoring of the Canton of Zürich and (b) cumulated DOC concentrations.

In order to bring the results of the column tests into a temporal context (assignment of L/S to time), the dataset is supplemented by simple emission prognosis modelling (Lauer et al., 2011). To define an annual change of L/S ($\Delta L/S$), the height of a deposit is linked with annual infiltration from precipitation, representing a simple approach to convert L/S to time. Parameters used for the model are based on measured average conditions from Swiss landfills (Table 3). Average density of deposited bottom ash is $1.6 \text{ m}^3/\text{t}$ (j_t) and average height of a deposit is 20 m (H). Average annual precipitation in Switzerland is 1.2 m, of which approximately 35 % infiltrates into a landfill, resulting in a quantity of leachate of $0.42 \text{ m}^3/\text{m}^2/\text{y}$ (S_w). The annual change of L/S is therefore $0.013 \text{ l/kg}\cdot\text{y}$ ($\Delta L/S$). For the heterogeneity factor (h), which describes the water flow in landfills, two scenarios have been chosen: (1) eluate test scenario with $h=1$, which neglects heterogeneity and represents a homogenous flow through a deposit, corresponding to the conditions of batch and column tests, (2) landfill scenario with $h=4$, which assumes high heterogeneity, where preferential flow paths dominate and only 25% of the deposit is percolated approximating conditions present in landfills.

The model for the eluate test scenario ($h=1$) is tested based on the evolution of DOC concentrations from the column tests. The initial concentration of readily soluble DOC (c_0) corresponds to 95 % of L/S 0.1 in the column test (Figure 4a), while the initial concentration of

persistent organic material is represented by the remaining 5 %. The readily mobilisable portion (m_v) equals to approximately 4 % TOC mobilised as DOC up to L/S 10, while the emission potential of persistent organic material (m_{org}) corresponds to the OC/TOC ratio of 33 %.

Table 3: Model parameters used for DOC based on column tests and estimated conditions from Swiss landfills.

Parameter	C_0 mg/l	C_{org} mg/l	m_v mg / kg	m_{org} mg C/ kg	S_w $m^3/m^2/y$	H m	j_t t/m^3	$\Delta L/S^*$ $l/kg*y$	h -
DOC	243	13	257	2250	0.42	20	1.60	0.013	1 and 4

* $\Delta L/S = S_w / (H * j_t)$

For the eluate test scenario with homogenous flow ($h=1$) the modelled concentration curve is within an error of 33 % from the measured concentration curve of the column test (Figure 5a). The strongest deviation of the modelled concentration from the measured values occurs between L/S 1-2 with an overestimation by the model of 33 % and between L/S 4-7 with an underestimation of 33 %. Both, measured and modelled DOC concentration suggest that DOC <20 mg/l is reached between L/S 3-4 corresponding to 300-400 years. Changing the model towards the landfill scenario with a heterogeneous flow regime ($h=4$) results in a more rapid decrease of DOC concentrations reaching concentrations <20 mg/l after 70 years (Figure 5b).

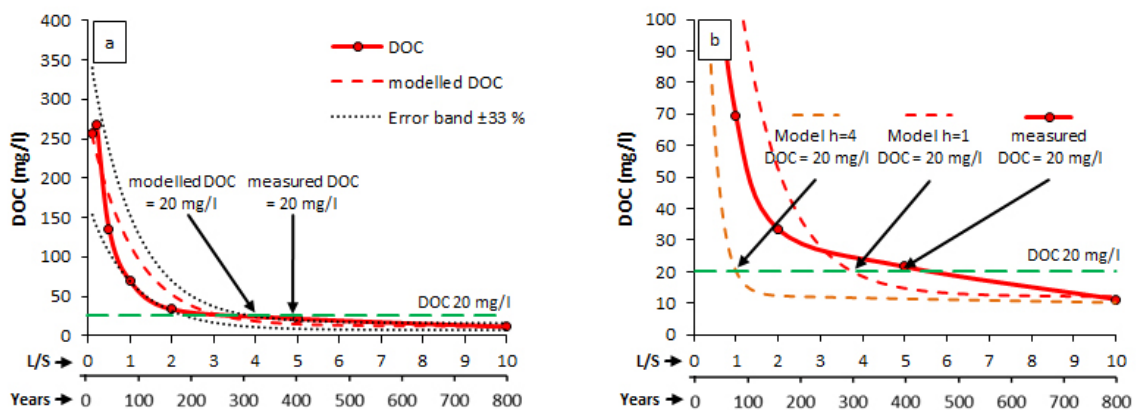


Figure 5: (a) Modelled concentrations for DOC corresponding to homogenous flow ($h=1$) in comparison with measurements from column test performed with bottom ash from four MSWI plants outside the monitoring of the Canton of Zürich. (b) measured concentration for DOC in column tests and modelled concentrations with heterogeneity factor $h=1$ and $h=4$, respectively.

4 Discussion

4.1 TOC as an indicator for burnout quality

Municipal solid waste with a typical mixture for the Canton of Zürich shows a trend towards lower TOC concentration in bottom ash over the years (Figure 2a). There are many reasons for this decrease and most of them depend on the operating strategy of MSWI plant operators. The concentration of TOC is mainly controlled by the burnout quality, which is influenced by the following factors (Koralewska, 2019): MSWI plant design, waste throughput (reduced bed thickness), fuel quality and homogeneity (moisture and calorific value), distribution and temperature of primary air ($>120^{\circ}\text{C}$), firing bed temperature, combustion control and discharge technology.

The result of optimised firing conditions is clearly visible for Plant A. The focus has been laid on optimised burnout quality since the beginning of the monitoring in 2008. Therefore, very low and steady TOC concentrations of bottom ash (<0.35 wt.-%) are reached reliably already before changing from wet to dry discharge. A pronounced decrease in TOC concentration of bottom ash of Plant E marks the implementation of dry discharge in 2016, combined with a waste shredder for all waste input and optimised primary air preheating (TOC values <0.35 wt.-%). However, similar improvements are achieved in Plant B and D demonstrating that also with wet discharge technology TOC concentrations 0.5 wt.-% are reached, which lie below the cantonal target value given by the environmental authority of the of Canton of Zürich. The implementation of dry discharge in Plant B in 2016 did not lead to an additional decrease in TOC concentration of bottom ash as has been shown at Plant E. The rather fluctuating TOC concentration of bottom ash in Plant C on a level above the cantonal target value demonstrates that optimisation measures have not been successful for this grate furnace so far. In order to meet the target value for TOC, it has been decided to optimise primary air preheating $>120^{\circ}\text{C}$, what has been shown as major factor to reduce TOC content of bottom

ash (Koralewska, 2019). Such measures would also be necessary in Plant F, where TOC concentration of bottom ash clearly exceed the cantonal target value. However, this plant has reached the end of its life cycle and will be shut down in spring 2021. Meanwhile, the focus is laid on district heating with waste from abroad.

In summary, it has been shown that in bottom ash originating from waste input of the Canton of Zürich (average calorific value of 12.2 MJ/kg), TOC concentrations of 0.5 wt.-% are reachable when the influencing firing options are optimised and managed in a stable manner, independent of discharge technology. Apart from these trends over a ten-year period, seasonal trends in TOC concentration of bottom ash can be observed. The most pronounced seasonality is present in bottom ash from Plant C with high TOC values (1–1.5 wt.-%) in winter and low TOC values (0.5-1 wt.-%) in summer. A reason for this might be the enhanced construction activity in summer, where more inorganic construction material in waste input leads to lower TOC concentrations in the bottom ash.

4.1.1 TOC vs. OC

Numerous studies prove that only the fraction of TOC consisting of organically bound carbon (OC) is degradable and bears a risk for mobilisation as DOC (Ferrari, 1997; van Zomeren and Comans, 2009). Therefore, risk assessment of bottom ash on landfills could focus on OC solely. However, as investigated by the environmental authority of the Canton of Zürich, at low concentration levels TOC is nonetheless a more reliable parameter for the evaluation of bottom ash regarding deposition with low aftercare. This has the following reasons (Koralewska, 2019): (1) The method for temperature-dependent combustion of carbon proves inaccurate for low concentrations of OC, due to insufficient reproducibility for the analysis of OC between different laboratories, but also for multiple determination. In fact OC concentrations (determined with temperature-dependent combustion) that correspond to

TOC concentrations <0.3 wt.-% (determined with a CHNS-analyser), are affected by this inaccuracy. As the cantonal target value for TOC is 0.5 wt.-%, corresponding OC concentrations lie in this critical range (Figure 3). (2) The concentration of OC that corresponds to the cantonal TOC target value of 0.5 wt.-% is 0.17 wt.-%. Today the limit of detection for OC with the method of temperature-dependent combustion is 0.1 wt.-%. For reliable measurements, however, the limit of detection should be 10 times lower (0.017 wt.-%) than the corresponding target value. The closer the target value lies at the limit of detection, the higher are unwanted effects of the matrix that influence the measurement uncertainty. Ultimately, the low correlation between TOC and OC (Figure 1b) may be due to these uncertainties. Thus, from today's point of view, TOC remains the parameter of choice for the determination of burnout quality in bottom ash.

4.2 Mobilising potential

4.2.1 Batch tests

Batch tests provide information on mobilising potential of contaminant load, relevant for the environmental impact of a hazardous substance. However, they show no temporal progression. On landfills, infiltrating water leads to a time-dependent increasing L/S-ratio with a heterogeneous flow regime characterised by preferential flow paths. For readily soluble, pH-independent constituents, the measured concentrations in the batch eluates indicate the maximum amount of substance that can be mobilised in an aqueous solution under equilibrium conditions. The solubility of heavy metals, however, is strongly pH-dependent and thus the measured concentrations are influenced by the pH conditions generated with neutral and CO₂-saturated water. The fraction of TOC mobilised as DOC from bottom ash is 4 % with an average concentration of 32 mg DOC/l (Table 2). The results of the batch tests show no correlation between TOC and DOC, neither for individual plants (max. R² = 0.24 for Plant D) nor

for the plants overall ($R^2 = 0.22$, Figure 1c). However, comparing TOC and DOC concentrations it is evident, that the cantonal target value for TOC concentration in bottom ash of 0.5 wt.-% leads to DOC concentrations <20 mg/l. This lies in the range of the threshold value for discharge of landfill leachate into surface water (10 mg/l DOC), according to the Swiss Water Protection Act (Figure 1c). Because OC contains mainly the readily soluble fraction of TOC, the average percentage of DOC mobilisation in respect to OC is 3.5 times higher (14 %). As for TOC and DOC there is no overall correlation between OC and DOC, however, the results can be split in two different levels for OC concentration (Figure 1d). The correlation between OC and DOC for the group with lower OC concentrations shows an $R^2 = 0.75$, while the second group with high OC concentrations shows an even better correlation ($R^2 = 0.93$). All values from this second group have in common that they derive from 2013. Whether there is a methodological problem within the OC measurements of this year leading to the observed anomaly is the subject of further investigations.

Ammonium is an ecotoxic constituent that derives from organic matter with an average eluate concentration of 3.1 mg/l (Table 2). Eh-pH diagrams, depicting the inorganic geochemical behaviour of elements, suggest that under the prevailing conditions ammonia (NH_3) should be the dominating N-species (Takeno, 2005). However, results of the monitoring show that in fact NH_4^+ dominates, mobilising on average 10 % of the total nitrogen in bottom ash. This is because complex microbial degradation and conversion processes in landfills break down proteins, the main nitrogen source contained in the waste, to NH_3 as well as NH_4^+ (Mayerhofer, 2017). Ammonium is mainly discharged via landfill leachate, while ammonia escapes via gas phase (Brandstätter et al., 2015). Thus, NH_4^+ and DOC concentrations in leachates are good indicators of the landfill stage and play a major role concerning the duration of the aftercare necessary for bottom ash landfills. They show a similar mobilisation behaviour for batch tests with a correlation of $R^2 = 0.58$ over all bottom ash eluates from the

monitored period (Figure 1e). While the mobilisation of DOC and NH_4^+ is relatively independent of the prevailing pH conditions, most heavy metals show a strong dependence on pH. At alkaline pH conditions usually present in leachates of bottom ash landfills in early stages, heavy metals possess very limited mobility and are sorbed on reactive surfaces. The relatively high concentrations of Cu (aq) are due to mobilisation via complexation with (in)organic ligands such as DOC. This process is attributed to a complex mixture of polymeric compounds referred to as humic and fulvic acids, which contain functional groups with several reactive complexing sites, which have the ability to bind trace elements by forming inorganic complexes (Aiken, 1985; Stevenson, 1994; Cavallino, 2017). Ultimately this leads to the correlation between DOC and Cu (aq) observed in Figure 1f ($R^2 = 0.66$).

Tests using CO_2 -eluate show that near neutral pH-conditions (average pH 6.9) result, corresponding to a future stage in landfills with reduced buffer capacity of the bottom ash. However, even at these conditions Cu (aq) ions are not yet mobilised. According to Dzombak and Morel (1990), a pH below 6.5 is necessary for Cu (aq) to be mobilised. Also the Cu-DOC complexing is of minor importance shown by an average concentration of Cu (aq + CO_2) of only $\frac{1}{3}$ of the average concentration of Cu (aq).

4.2.2 Column tests and modelling approach

The comparison of DOC results from the batch test according to the Swiss Waste Ordinance (32 mg/l) with those from the European column tests according to CEN TS 14405 (28 mg/l) show similar cumulative concentrations at L/S 10 (Table 2, Figure 4b). Thus, batch tests provide accurate information on the available quantity of a specific constituent mobilised at L/S 10, while column tests additionally show the dynamics of the constituent release (Figure 4a).

In terms of concentration development for the eluate test scenario with homogeneous flow regime ($h=1$), the modelled concentration lies within 33 % of the measured DOC concentra-

tions in the column test (Figure 5a). Although a simple approach was taken using an exponential decrease the model is considered suitable to estimate DOC concentrations. This is also shown by the calculated duration of aftercare for both column test and model approach, where DOC <20 mg/l is reached between L/S 4-5, corresponding to 300-400 years. Moreover, the applied modelling approach provides valuable insights to the differences of leaching tests and natural systems in terms of flow regime. Homogenous flow through the material ($h=1$), as is simulated with the batch and column test, represents a “worst case” simulation for maximal concentration and aftercare. However, homogeneous leaching on landfills hardly ever occurs due to preferential flow paths. Changing the model towards more heterogeneity ($h=4$) results in only parts of the material being leached. This leads to lower mobilisation of pollutants in landfills and thus to faster decreasing DOC concentrations in the leachates (Figure 5b). With this landfill scenario DOC concentrations <20 mg/l are reached in approximately $\frac{1}{4}$ of the aftercare time compared to homogenous flow conditions of the eluate test scenario. Consequently, partial leaching of landfilled material results in a higher remaining DOC reservoir bearing the potential of future DOC emissions due to changing preferential flow paths through new areas.

5 Conclusions

The results presented in this study highlight that reducing TOC contents in bottom ash is important in order to minimise emission potential and duration of aftercare of bottom ash landfills. In the Canton of Zürich, TOC concentration in bottom ash has been reduced by 50 % from 2008 – 2018. This has been achieved thanks to a target value for TOC concentration in bottom ash of 0.5 wt.-%, which has been defined in 2008 by the environmental authority of the Canton of Zürich together with the MSWI plants. The target value has been defined for TOC, even though OC is more relevant for the mobilisation of DOC. Comparative measurements have shown that TOC at low values ($\ll 0.5$ wt.-%) is a more reliable parameter for the assessment of burnout quality and emission potential of bottom ash. In comparison, OC shows analytical uncertainties at low concentrations.

The monitoring of six MSWI plants highlights the effects of decreasing TOC concentrations on the environmentally relevant constituents DOC, NH_4^+ and Cu (aq). TOC partly controls the emission of DOC and consequently the mobilisation of Cu (aq) in leachates from bottom ash at early stages. TOC therefore plays an important role for the environmental impact and emissions of bottom ash landfills. In addition, NH_4^+ in bottom ash also derives from organic constituents and shares a similar emission behaviour as DOC. On average 4 % of the TOC and 10 % of the nitrogen is mobilised with batch eluate tests according to Swiss Waste Legislation, resulting in average concentration of 32 mg DOC/l and 3 mg NH_4^+ /l. TOC contents of bottom ash < 0.5 wt.-%, complying with the cantonal target value, lead to DOC concentrations < 20 mg/l. This lies in the range of the threshold value for discharge of landfill leachate into surface waters (10 mg DOC/l), according to the Swiss Water Protection Act. The comparison with dynamic column tests has shown, that batch tests are accurate enough for the evaluation of bottom ash quality. However, simple modelling has shown that different flow regimes prevail in eluate tests and landfills. Due to the homogenous flow in eluate tests, DOC concentrations

generally are higher than in landfills where heterogeneous flow is characteristic. However, chemical and biological changes such as decreasing pH conditions due to the change of acid buffer capacity, change of temperature, redox-processes, sorption and microbial degradation of organic compounds significantly influence the leaching behaviour of landfilled bottom ash. Thus, to enhance the accuracy of the model and especially for the prediction of heavy metal release further studies with more sophisticated reactive transport models are necessary.

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Figure and Table Captions

Figure 1: Correlations of concentrations in bottom ash between (a) TOC and TC, (b) TOC and OC, (c) TOC and DOC, (d) OC and DOC, (e) NH_4^+ and DOC and (f) Cu (aq) and DOC during the monitored period from 2008–2015.

Figure 2: Temporal evolution of (a) TOC concentrations in bottom ash and (b) DOC concentrations in eluates from batch tests for the monitored Plants A–F.

Figure 3: Proportions of TIC (green), EC (blue) and OC (red) in bottom ash per plant for the period from 2011–2013.

Figure 4: (a) Average DOC concentrations at specified L/S ratios measured in column tests performed with bottom ash from four MSWI plants outside the monitoring of the Canton of Zürich and (b) cumulated DOC concentrations.

Figure 5: (a) Modelled concentrations for DOC corresponding to homogenous flow ($h=1$) in comparison with measurements from column test performed with bottom ash from four MSWI plants outside the monitoring of the Canton of Zürich. (b) measured concentration for DOC in column tests and modelled concentrations with heterogeneity factor $h=1$ and $h=4$, respectively.

Table 1: Technical details and applied changes of investigated MSWI plants during the monitoring time.

Table 2: Concentration of specific constituents and pH of batch eluate Test 1 and Test 2 of bottom ashes from Plant A–F over the monitoring period (2008-2018). Number of measurements (N), average (\emptyset), median, minimum, maximum concentration and number of outliers ($\downarrow = <1.5 \cdot \text{IQR}$, $\uparrow = >1.5 \cdot \text{IQR}$).

Table 3: Model parameters used for DOC based on column tests and estimated conditions from Swiss landfills.