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Using multivariate regression modeling for sampling and predicting chemical characteristics of mixed waste in old landfills

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ABSTRACT

Municipal solid waste landfills pose a threat on environment and human health, especially old landfills which lack facilities for collection and treatment of landfill gas and leachate. Consequently, missing information about emission flows prevent site-specific environmental risk assessments. To overcome this gap, the combination of waste sampling and analysis with statistical modeling is one option for estimating present and future emission potentials. Optimizing the tradeoff between investigation costs and reliable results requires knowledge about both: the number of samples to be taken and variables to be analyzed.

This article aims to identify the optimized number of waste samples and variables in order to predict a larger set of variables. Therefore, we introduce a multivariate linear regression model and tested the applicability by usage of two case studies. Landfill A was used to set up and calibrate the model based on 50 waste samples and twelve variables. The calibrated model was applied to Landfill B including 36 waste samples and twelve variables with four predictor variables.

The case study results are twofold: first, the reliable and accurate prediction of the twelve variables can be achieved with the knowledge of four predictor variables (Loi, EC, pH and Cl). For the second Landfill B, only ten full measurements would be needed for a reliable prediction of most response variables. The four predictor variables would exhibit comparably low analytical costs in comparison to the full set of measurements. This cost reduction could be used to increase the number of samples yielding an improved understanding of the spatial waste heterogeneity in landfills.

Concluding, the future application of the developed model potentially improves the reliability of predicted emission potentials. The model could become a standard screening tool for old landfills if its applicability and reliability would be tested in additional case studies.

1. Introduction

Municipal solid waste (MSW) landfills pose a long-term threat to human health and environment via leachate and gaseous emissions. The source of these emissions, the solid body of landfills is typically not very well examined. This is especially the case for older MSW-landfills, where no documentation about the deposited material is available. For assessing the long-term emission potential, the highly heterogeneous solid body composition is of major interest. The emissions eventually derive from the solid body, which particularly applies for gas production (Barlaz et al., 1990).

The lack of information concerning the landfilled waste is related to high sampling and chemical analytical costs. Furthermore, the extracted information of such solid waste sampling campaigns is limited, since the heterogeneity of the landfill body typically overshadows the results (e.g. Östman et al., 2006). In comparison to solid waste sampling, leachate sampling campaigns are more common, mainly because leachate is easier to access and also directly related to groundwater pollution (Eggen et al., 2010). However, leachate also strongly varies in its composition within a landfill spatiotemporally (Kjeldsen et al., 2002) and at most older landfill sites leachate cannot be collected as they are not equipped with a base lining system.

Abbreviations: BOD_5, biological oxygen demand after 5 days; COD, chemical oxygen demand; DW, dry weight; EC, electrical conductivity; ICP-AES, inductively coupled plasma atomic emission spectroscopy; Loi, loss on ignition; MSW, municipal solid waste; RI_4, respiration index after 4 days; RMdSPE, root median square percentage error; SD, standard deviation; sqrt, square root; TN, total nitrogen; TOC, total organic carbon; WC, water content.

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Typical sampling campaigns of MSW-landfills, as rarely as they are conducted, lead to 20–40 valid samples (Mor et al., 2006; Sormunen et al., 2008), where a wide range of analytical procedures in view of emission potential is applied. According to the Austrian standard ON S 2087, a guideline for the investigation of contaminated sites such as old landfills, in standard situations eight solid variables should be analyzed for as well as twelve variables after elution. Measuring twenty variables would lead to high analytical costs per sample. According to this guideline, it is recommended to take samples every 20 × 20 m. In view of landfill heterogeneity, we propose to take a larger number of samples and measuring less variables. This would ideally lead to an improved understanding of the emission source and enable site administrators to better identify for example hot spots of organic matter.

The aim of this article hence is to identify the optimized number of waste samples and chemical variables in order to predict a larger set of chemical variables. To achieve this goal, we applied a linear multivariate model based on four selected predictor variables with low analytical costs (Loi (loss on ignition), pH, EC (electrical conductivity) and Cl (Chloride)). By that we obtained predictions about twelve response variables for two fairly differing landfills.

2. Material and methods

In this work, we present a multivariate linear model. The model was formulated in the view of low analytical costs and with data from Landfill A. To show that the model can be applied to other MSW-landfills as well, the resulting model coefficients were applied on data from a second Landfill B. Afterwards, the model outcome was adjusted as will be explained below. For the sake of clarity we provide a short glossary with the most crucial statistical terms in the context of this article:

Variable: Method of measurement (e.g. Loi, TOC, WC); column in a typical dataset.
Observation: The measured values for every variable of one sample; row in a typical dataset.
Predictor variable: Variables used for prediction (here: Loi, pH, EC and Cl).
Response variable: The predicted variable (here by applying multilinear modeling).
Model adjustment criterion: Maximum 10% RMdSPE deviation from adjustment based on all measured variables.
Model evaluation criterion: Maximum 35% RMdSPE deviation predicted vs. measured.

2.1. Site characteristics and sampling

2.1.1. Landfill A

Landfill A contains approximately 220,000 m^3 (fresh matter) of waste with an average deposition height of 3.7 m. According to test pitting conducted the landfilled waste mainly consists of MSW (66% moist mass), excavated soil (18% moist mass) and construction and demolition waste (16% moist mass). Landfilling took place at the site from 1965 to 1974 and resulted in a total landfill volume of approximately 240,000 m^3 including top soil (Brandstätter et al., 2013).

2.1.2. Landfill B

At Landfill B about 210,000 m^3 (fresh matter) of untreated municipal and commercial solid waste have been deposited between 1976 and 1995 (Prantl, 2007; Prantl et al., 2006a,b). The site is characterized by an average waste depth of 7.7 m and is divided into two sections differing in reactivity and age. The waste samples analyzed for this article originate from both sections.

2.1.3. Sampling

Sampling and chemical analyses of the deposited waste at Landfill A were conducted by the authors of the present study, while information about Landfill B was obtained from the literature (Prantl, 2007; Prantl et al., 2006a,b). At both landfills the excavated material was sieved with a mesh width of 20 mm. For the sampling campaign in Landfill A an excavator and for Landfill B a grab-excavator with 600 mm diameter was used. The average sample size in both cases was ~20 kg. At Landfill A in total 56 samples from 17 pits were taken and at Landfill B 54 samples from 20 excavated holes. For the sampling campaign in Landfill A, a priori information about the distribution of organic matter in the landfill was available (unpublished study), performed after the evaluation of a risk assessment study from the Austrian environmental agency (Environmental Agency Austria, 2005). Based on this information, the herein described sampling campaign at Landfill A focused on zones rather rich in organics.

2.2. Chemical analyses

This section provides additional information to Table 1 which contains the applied analytical devices and/or the standardized methods.

2.2.1. Solids

For chemical extraction of Cr_s, Cu_s, Pb_s and Zn_s in Landfill A, a microwave oven (Start 1500, MLS GmbH, Leutkirch Germany) was used (200 °C). The applied solvent was aqua regia (HCl and HNO_3 in the volumetric ratio of 3:1). The analysis of the elemental content was performed with inductively coupled plasma atomic emission spectroscopy (ICP-AES Ultima 2, Horiba Jobin Yvon, Munich, Germany). The RI_4 (respiration index after 4 days) of solid waste samples taken from Landfill A was analyzed by Agrolab Austria GmbH and for samples of Landfill B it was determined according to Binner and Zach (1999).

2.2.2. Eluate

For eluting the fresh waste material a water/solid ratio of 10 l/kg was applied for both landfills. The material was eluted in an orbital shaker at 250 rpm for 24 h at room temperature. For Landfill A, the EC and pH were measured with a pH meter (Seven Excellence S470 kit, Mettler Toledo, Ohio, USA) and the variables Cl and SO_4 were analyzed using ionic chromatography (IC Dionex ICS 900, ThermoFisher Scientific Inc., Massachusetts, USA).

2.3. Statistical analyses

2.3.1. Data selection with plausibility tests

All statistical analyses were performed with the program R (ver. 3.0.1, R Core Team, 2013). For selecting plausible data from the full datasets we applied two reproducible criteria on data of each of the landfills: the first criterion was that the ratio of Loi and TOC_s (total organic carbon; total carbon – total inorganic carbon) should be lower than 2.4. The second criterion was that the ratio of TOC_s and TN should be higher than 8.

The reasoning behind the first criterion was that when investigating the ratio of Loi and TOC_s for organic substances present in landfills (such as glucose, cellulose, lignin, fats, protein or different plastic polymers), this ratio can theoretically vary between 2.5 for glucose (cellulose, hemicellulose and lignin show a ratio of 2.25, 2.31 and 1.5, respectively) and 1.08 for polystyrol, while polyethylene and polypropylene are characterized by a ratio of 1.17 (Kost, 2001)). A table indicating TOC:TN values of different polymers is given in supplementary material (Appendix 1). Taking possible measurement errors into account as well as the fact that there will be always a mixture of different organic substances in landfills

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Table 1
Chemical analyses.

Landfill	A		B		
Parameter	Method	Device	Method	Device	Source
Preparation					
Milling	Ball mill		Centrifugal mill		a
Sieving	0.5 mm Mesh width		0.63 mm Mesh width		a
Solids					
WC	105 °C, 24 h	Drying chamber	105 °C, 24 h	Drying chamber	a
Loi	550 °C	Muffle furnace	545 °C	–	a
TOC_s	TC-TIC	Macro CHNS	TC-TIC	Variomax CNS analyser	a
TN_s	–	Macro CHNS	–	Variomax CNS analyser	a
Cr_s	Aqua regia extraction	ICP-AES	ON EN ISO 11885	–	b
Cu_s	Aqua regia extraction	ICP-AES	ON EN ISO 11885	–	b
Pb_s	Aqua regia extraction	ICP-AES	ON EN ISO 11885	–	b
Zn_s	Aqua regia extraction	ICP-AES	ON EN ISO 11885	–	b
RI_4	ON S 2027-1	–	–	Voith Sulzer sapromat	a
Eluted					
EC	–	Seven excellence S470	ON M 27888	–	c
pH	–	Seven excellence S470	ON EN 6244	–	c
NH_4–N	DIN EN ISO 11732	–	DIN EN ISO 11732	–	a
Cl	–	Dionex ICS 900	ON EN ISO 15682	–	b
SO_4	–	Dionex ICS 900	ON EN ISO 10304-1	–	b
COD	DIN 38409-43	–	ON M 6265	–	a
BOD_5	DIN EN 1899-1	–	ON M 6277	–	c

Notes: Sources: a: Prantl et al., 2006a,b; b: Prantl et al., 2006a,b (Project Interland); c: Prantl, 2007. The subscripted suffix s stands for solid. The italic parameters were used as independent variables for the linear models. BOD_5, biological oxygen demand; COD, chemical oxygen demand; DW, dry weight; EC, electrical conductivity; Loi, loss on ignition; TN, total nitrogen; RI_4, respiration index after 4 days; TOC, total organic carbon.

present, we applied a maximum ratio of 2.4. Potential errors could derive from either the measurements of Loi or TOC. The Loi could be overestimated, if the sample is not absolutely dry and the TOC being calculated based on two measurements is subject to two potential analytical error sources. The measurement values of the excluded samples are listed in summarized in supplementary material (Appendix 2).

The reasoning behind the second criterion was that the ratio of TOC:TN in landfilled MSW would be never go below the TOC:TN ratio found in microbial biomass, assuming that proteins (about 3:1) and nylon (about 5.1:1) are not the dominant organic compounds in MSW. During the sampling campaign at Landfill A we found some nylon tissue, but this was not the main plastic source. In addition nylon was to a large extent removed during sieving. For old waste material it is unlikely, that available proteins have not been incorporated to microbial biomass or mineralized.

According to Cleveland and Liptzin (2007) the average (geometric mean) molar C:N ratio in microbial biomass of soil microbes was 8.6 based on 48 published sources. Soil as a habitat shows many commonalities to landfills, like e.g. an organic matrix (humic substances) and alternating CO_2 and O_2 soil gas concentrations. Transferred to mass ratios this molar C:N ratio in microbes would result in a TOC:TON ratio of 7.4. Including potential measurement errors and taking into account potential flexibility of soil microorganisms we defined this criterion rather tolerant with 8:1 (TOC:TN) or higher.

In total, analytical results of six samples out of 56 from the dataset of Landfill A failed on the first criterion, and 18 samples out of 54 from Landfill B. Applying the second criterion did not result in the removal of any samples.

2.3.2. Statistical testing

As a test for normality, Shapiro–Wilk-Test (S–W-test) was chosen, since it is considered to be the most powerful in comparison to other typically applied normality tests (Razali and Wah, 2011). If the *p*-value was higher than 0.05, the distribution was not considered to be significantly different from a normal distribution in accordance with other standard test procedures of normality (Lizik et al., 2013). For testing of significant differences between two groups, either the parametric *t*-test (for normally distributed data, mean) or otherwise the non-parametric Mann–Whitney-*U*-test (median) was applied. Even though we are aware of the fact, that linear regression is sensitive to outliers, we did not transform the data prior to performing linear regression. Firstly, transformation procedures did not improve the outcome drastically (data not shown), secondly the interpretation of the results would have been more complicated, and thirdly the practical application of the presented model would be more difficult. Instead we applied the above mentioned criteria for data selection to remove potential implausible data.

2.3.3. Statistical modeling

2.3.3.1. Model formation. We selected four predictor variables for describing the remaining response variables with multiple linear regression analysis. We selected these four variables in view of gaining the maximum information about the chemical composition with minimum measurement effort. The four predictor variables were: Loi, pH, EC and Cl. The mathematical formulation of the model is as follows (Weisberg, 2014, pp. 50):

$$y_p = D + a * \mathrm{Loi} + b * \mathrm{pH} + c * \mathrm{EC} + d * \mathrm{Cl} \quad (1)$$

with y_p as the respective response variable, D as the intercept and a, b, c and d as coefficients. The units of the predictor variables are given in Table 3. We calculated the model with data from Landfill A and applied the model to Landfill B. After model application we adjusted the model to improve the prediction as will be explained in 2.3.3.1 Step 3.

2.3.3.2. Model cycle. An overview of the model cycle and its five modeling steps is given in Fig. 1. The individual steps of the model cycle will be explained below.

Step 1 – Model building

The formulated model was calculated with data from Landfill A. As already described, we used the four predictor variables Loi, pH, EC and Cl for modeling of the respective response variables.

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Table 2
Regression coefficients from the calibration model of Landfill A.

Parameter	r^2	Intercept Coefficient		Loi *a*		EC *b*		pH *c*		Cl *d*	
Solids											
WC	0.56	14.6	ns	1.17	***	−2.05	*	−0.44	ns	0.001	ns
TOC_s	0.97	−3.41	–	0.60	***	0.12	ns	0.33	ns	0.000	ns
TN_s	0.78	0.25	ns	0.02	****	0.02	*	−0.03	ns	0.000	ns
Cr_s	0.13	−270	ns	5.24	–	−15.4	ns	42.5	ns	0.003	ns
Cu_s	0.12	−1712	ns	30.0	–	5.04	ns	231	ns	−0.008	ns
Pb_s	0.34	−1112	ns	57.3	***	19.7	ns	131	ns	−0.353	–
Zn_s	0.32	−3284	ns	76.8	**	74.8	ns	437	ns	0.127	ns
RI_4	0.16	14.6	*	−0.11	–	0.15	ns	−1.40	–	0.001	ns
Eluted											
NH_4–N	0.71	−227	ns	4.21	ns	−11.0	ns	31.9	ns	0.65	***
SO_4	0.66	−16,418	*	158	–	3946	***	1816	–	−3.68	*
COD	0.76	44,775	***	−435	**	3758	***	−6014	***	11.8	***
BOD_5	0.73	27,684	**	−290	**	2936	***	−3828	**	8.08	***

Notes: The corresponding units are presented in Table 3. The subscripted suffix s stands for solid. Significance levels: (ns $p > 0.1$; $p < 0.1$; $^{*}p < 0.05$; $^{**}p < 0.01$; $^{***}p < 0.001$). BOD_5, biological oxygen demand; COD, chemical oxygen demand; DW, dry weight; EC, electrical conductivity; Loi, loss on ignition; TN, total nitrogen; RI_4, respiration index after 4 days; TOC, total organic carbon.

Table 3
Results of the model application.

	Units	r^2	Non-adjusted RMdSPE (% measured)	Adjusted ($n = 10$) RMdSPE (% measured)
Solids				
WC	(% DW)	0.45	13.5	11.2
TOC_s	(% DW)	0.87	19.0	6.3
TN_s	(% DW)	0.69	26.4	13.2
Cr_s	(mg kg^{-1} DW)	0.36	387	25.4
Cu_s	(mg kg^{-1} DW)	0.10	219	26.1
Pb_s	(mg kg^{-1} DW)	0.08	264	31
Zn_s	(mg kg^{-1} DW)	0.19	183	61.7
RI_4	(mg O_2 g^{-1} DW)	0.00	40.7	31.8
Eluted				
NH_4–N	(mg kg^{-1} DW)	0.73	16.2	11.8
SO_4	(mg kg^{-1} DW)	0.04	162	251.1
COD	(mg O_2 kg^{-1} DW)	0.57	78.3	26.9
BOD_5	(mg O_2 kg^{-1} DW)	0.57	127	25.6

Notes: The values are based on the measurements of Landfill B. All numbers have been rounded to three significant figures. The subscripted suffix s stands for solid. BOD_5, biological oxygen demand; COD, chemical oxygen demand; DW, dry weight; EC, electrical conductivity; Loi, loss on ignition; LF, landfill; TN, total nitrogen; RI_4, respiration index after 4 days; RMdSPE, root-median square percentage error; TOC, total organic carbon; WC, water content.

Step 2 – Application of the model

The calculated model was applied on data from Landfill B. This is shown in Fig. 1 Step 2, application – red[1] triangles.

Step 3 – Model calibration

Model adjustment

Since the considered landfills differ in many aspects (see Fig. 2), it was necessary to adjust the model results. For adjustment a simple (univariate) linear regression was performed. We used the predicted values from the multilinear model as predictor variable and the measured values as response variable. This means, that here the regression had to be reversed. The resulting coefficients from this second regression analysis (intercept and slope) would then be applied on the unadjusted model values.

For estimating the amount of observations needed for a reasonably good model adjustment we used bootstrapping for cross-validating. Typically a bootstrap sample is obtained by randomly sampling n times, with replacement, from the original data points (Efron and Tibshirani, 1994). Replacement would mean that e.g. the same variable could be drawn twice. This bootstrapping was performed for an increasing amount of observations for each predicted variable. One prerequisite for this procedure would be a goodness of fit criterion of the model result to assess the output quality.

Goodness of fit criterion

The model adjusting would not affect the typically applied coefficient of determination (r^2) because all the predicted values from each variable are adjusted with the same coefficients. Therefore we applied a different criterion for evaluating the final model result. For comparing the model output prior to and after adjustment we used the root median square percentage error (RMdSPE, Hyndman and Koehler, 2006). This criterion was chosen for maximum comparability between different variables, since it is based on percentage errors and the RMdSPE is considered to be less sensitive to outliers than others based on the arithmetic mean. The criterion describes the deviation between the measured and the predicted values.

The following equations were adapted in agreement with Hyndman and Koehler (2006). The percentage error (PE) is given as:

$$PE_i = \frac{100 * (yp_i - ym_i)}{ym_i} \quad (2)$$

with i as index for each point and yp_i as the predicted values and ym_i as the measured values.

And the RMdSPE as:

$$RMdSPE = \sqrt{median(PE_i^2)} \quad (3)$$

Bootstrapping

After defining the quality criterion RMdSPE we investigated the necessary amount of measured response variables of Landfill B to obtain a reasonably good adjustment of the applied model to fit the measured data accurately.

Here we applied a bootstrapping procedure to estimate, how many observations would be needed to gain a reasonably good adjustment function and consequently model output. For every

[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

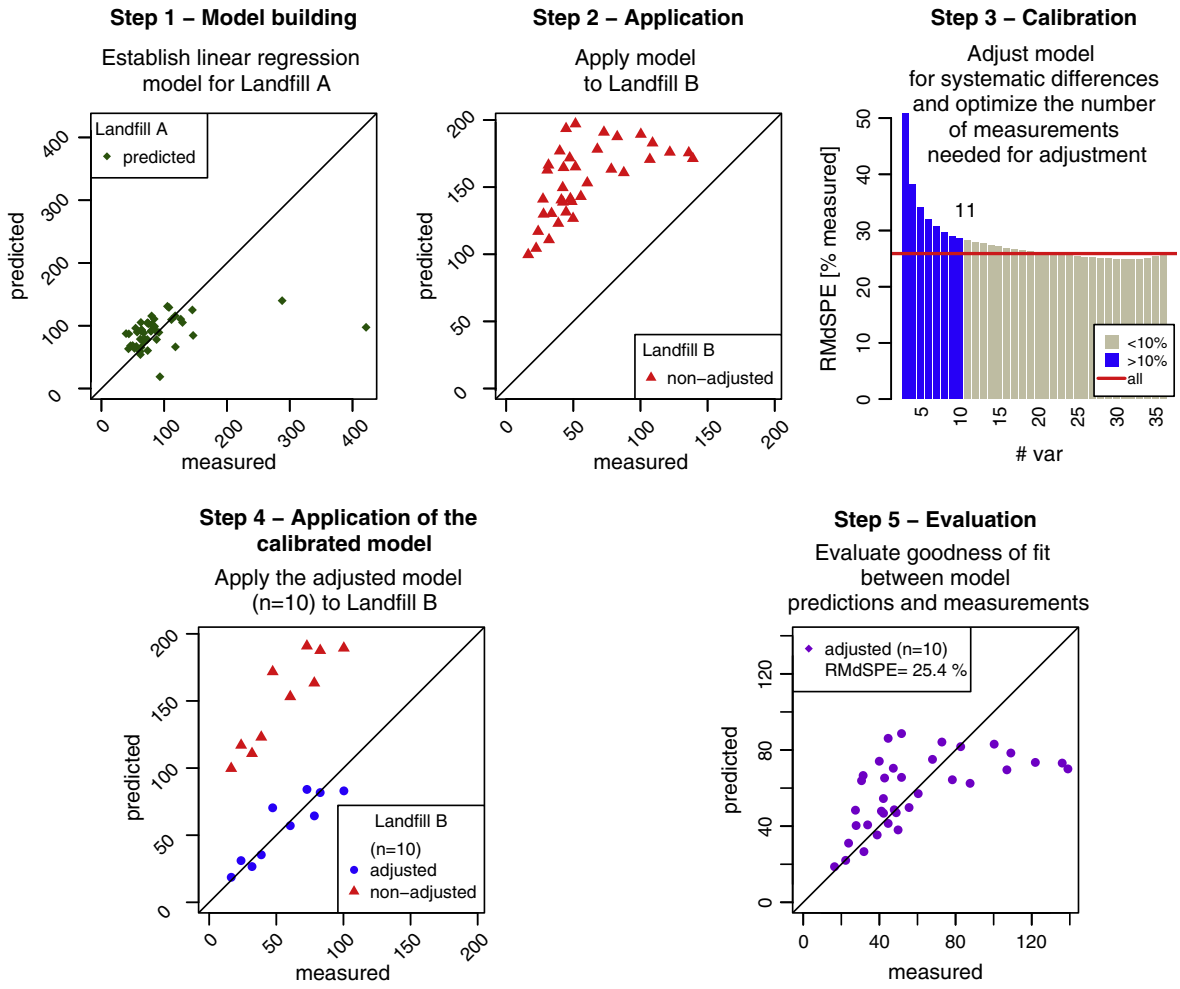

Fig. 1. Graphical overview of the model cycle. *Notes:* RMdSPE, root-median square percentage error.

bootstrap subsample we first predicted the response variable of Landfill B with the model from Landfill A (Step 2). Next we applied the model adjustment for every subsample, with the corresponding subsample of the non-adjusted prediction. This resulted in adjusted model values for each subset, of which we then calculated the RMdSPE.

In total we created 5000 bootstrap-subsamples from each response variable, for an increasing amount of observations with ($n = \{3 \ldots 36\}$) instead for the full dataset as is typically performed in bootstrapping. We started from three values, since the application of linear regression based on two data points was not considered as reliable. We then calculated the arithmetic mean from each bootstrapping with 5000 subsamples resulting in 34 values (3...36) per response variable.

The arithmetic mean of all RMdSPE results for each amount of drawn variables (=5000 (bootstrap replicates) * 3...36 (variables selected) * 12 (response variables)) was compared to the prediction based on the model adjustment using all observations of the response variables. We arbitrarily considered a difference between the errors from the bootstrap subsamples and from the errors of the whole dataset below 10% as sufficiently accurate for determining the amount of observations needed for adjusting the model (Model adjustment criterion).

Because of our study design, we applied bootstrapping without replacement. Performing linear regression with two exactly same values would not be reasonable. So, even if between-sample correlation would be higher without replacement than with replacement (Stephenson et al., 2010), we chose to apply bootstrapping without replacement to investigate how many measured values would be needed.

Step 4 – Application of calibrated model

Anticipating the results, for the majority of response variables the selection of ten observations would suffice to fulfill our predefined model adjustment criterion. So we performed the adjustment using ten randomly selected observations of Landfill B.

Step 5 – Model evaluation

The result of the unadjusted model ($n = 36$) was finally adjusted with univariate linear regression based on the previously selected ten observations ($n = 10$) in analogy to Step 3 model adjustment. The quality of the model result was assessed with the RMdSPE. For the goodness of fit criterion of the multilinear model we defined that everything below 35% of RMDSPE deviation from the measured observations would be considered as accurate (model evaluation criterion).

3. Results

3.1. Solid body analysis

The analytical results of the solid waste sampling are summarized in Fig. 2.

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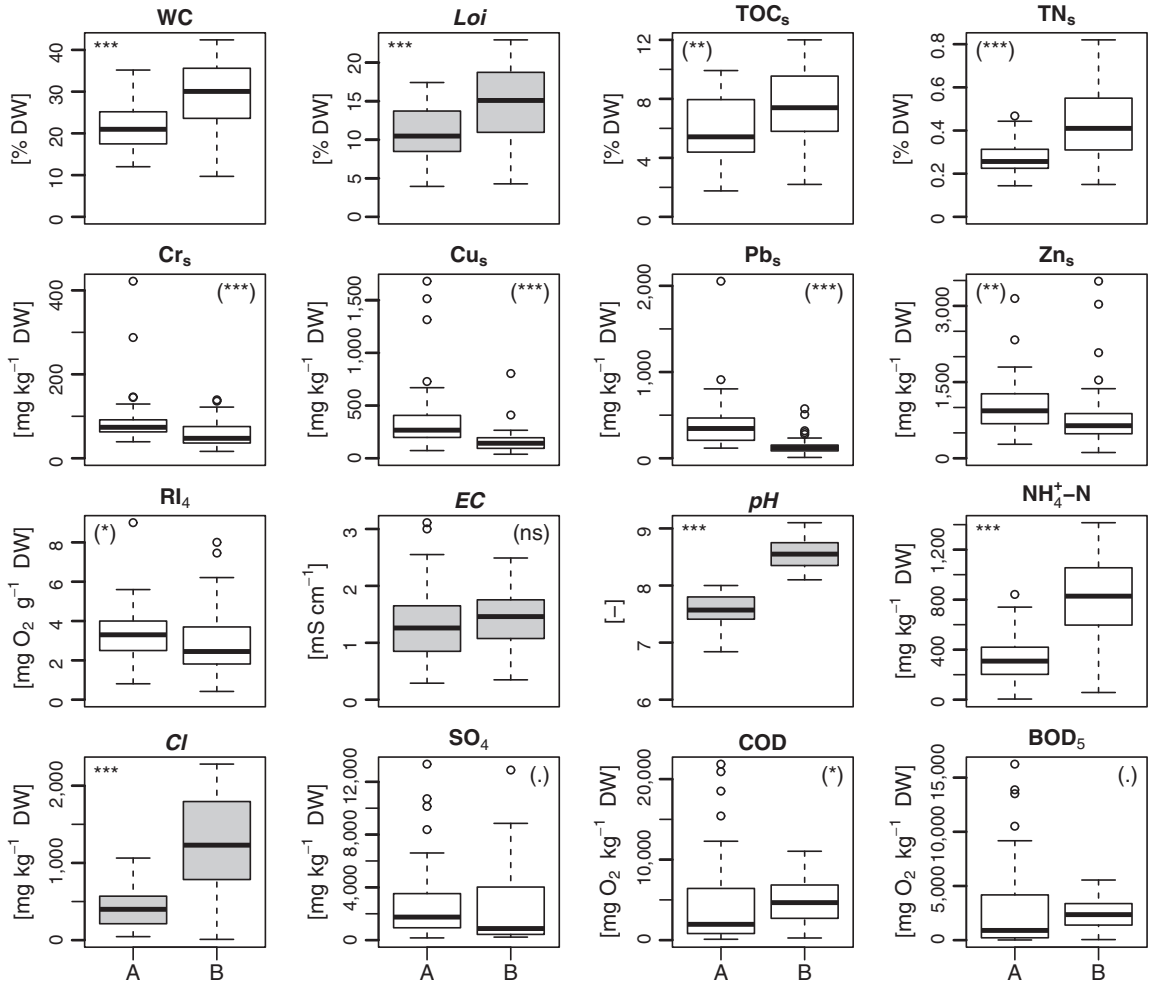

Fig. 2. Overall comparison between Landfill A and B. *Notes:* Boundaries of the box plots with the bold line representing the median indicate the 25th and 75th percentiles; whiskers have a maximum length of 1.5-fold interquartile range. Circles are outlying points. The gray scaled variables were used as predictor variables for the linear models. If one of the groups was considered as not normally distributed (significant Shapiro–Wilks test), Mann–Whitney *U*-test was applied for testing between the landfills (indicated by brackets), else a Student *t*-test. Significance levels: (ns $p > 0.1$; $p < 0.1$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$). The subscripted suffix s stands for solid. BOD_5, biological oxygen demand; COD, chemical oxygen demand; DW, dry weight; EC, electrical conductivity; Loi, loss on ignition; TN, total nitrogen; RI_4, respiration index after 4 days; SD, standard deviation; TOC, total organic carbon.

The two different landfills showed significant differences in nearly all variables, except for EC, SO_4 and BOD_5. The variables Loi, TOC_s, TN, NH_4–N, Cl and COD, typically considered as correlated with organic matter (except for Cl) were significantly higher in Landfill B. The pH however was significantly higher in Landfill B than in Landfill A and the BOD_5 did not differ significantly. Generally Landfill B had a higher MSW-content, but the sampling campaign of Landfill A targeted at sections high in organics. This sampling approach resulted in four high outlying values in COD and BOD_5.

The statistical distribution of the variables varied drastically as it is typical for landfill samples. In Landfill B four variables showed a more equal distribution than in Landfill A (S–W-test, TOC_s, TN, COD and BOD_5).

3.2. Linear regression model for Landfill A

We applied the multivariate linear model (Loi, EC, pH and Cl) on Landfill A for twelve response variables. As can be estimated by the coefficients from Table 2 the solid variables were mainly influenced by Loi whereas the eluted variables by EC, pH and Cl, but also by Loi. The metal contents and the RI_4 could be explained the least ($r^2 < 0.4$), while all the other variables showed a rather good fit ($r^2 > 0.65$), except for WC which was mediocre ($r^2 = 0.56$).

In Fig. 3, the model results are shown graphically by comparing measured and predicted values. In the *xy*-plots for the modeling results (Figs. 3 and 5), we applied the same range for the *x*- and *y*-axes. The model results from the metal contents as well as from the RI_4 are influenced by a few high outlying values.

3.3. Prediction of dependent variables for Landfill B

The results of the non-adjusted predicted model are shown in Table 3 (left result column) and Fig. 4. Similar to the calibration model, r^2 was low for the metal contents as well as for RI_4. The best predictions were achieved for TOC_s, NH_4 and TN_s, followed by BOD_5 and COD. We could not produce a reasonable fit for SO_4 and the WC was mediocre as before ($r^2 = 0.45$). For the non-adjusted model results of WC, TOC_s, TN_s and NH_4–N the accuracy criterion RMdSPE was below 30%, while for the metals it was above 180%. The eluted variables except for NH_4–N also showed a high RMdSPE (78.3% for COD, 127% for BOD_5 and 162% for SO_4).

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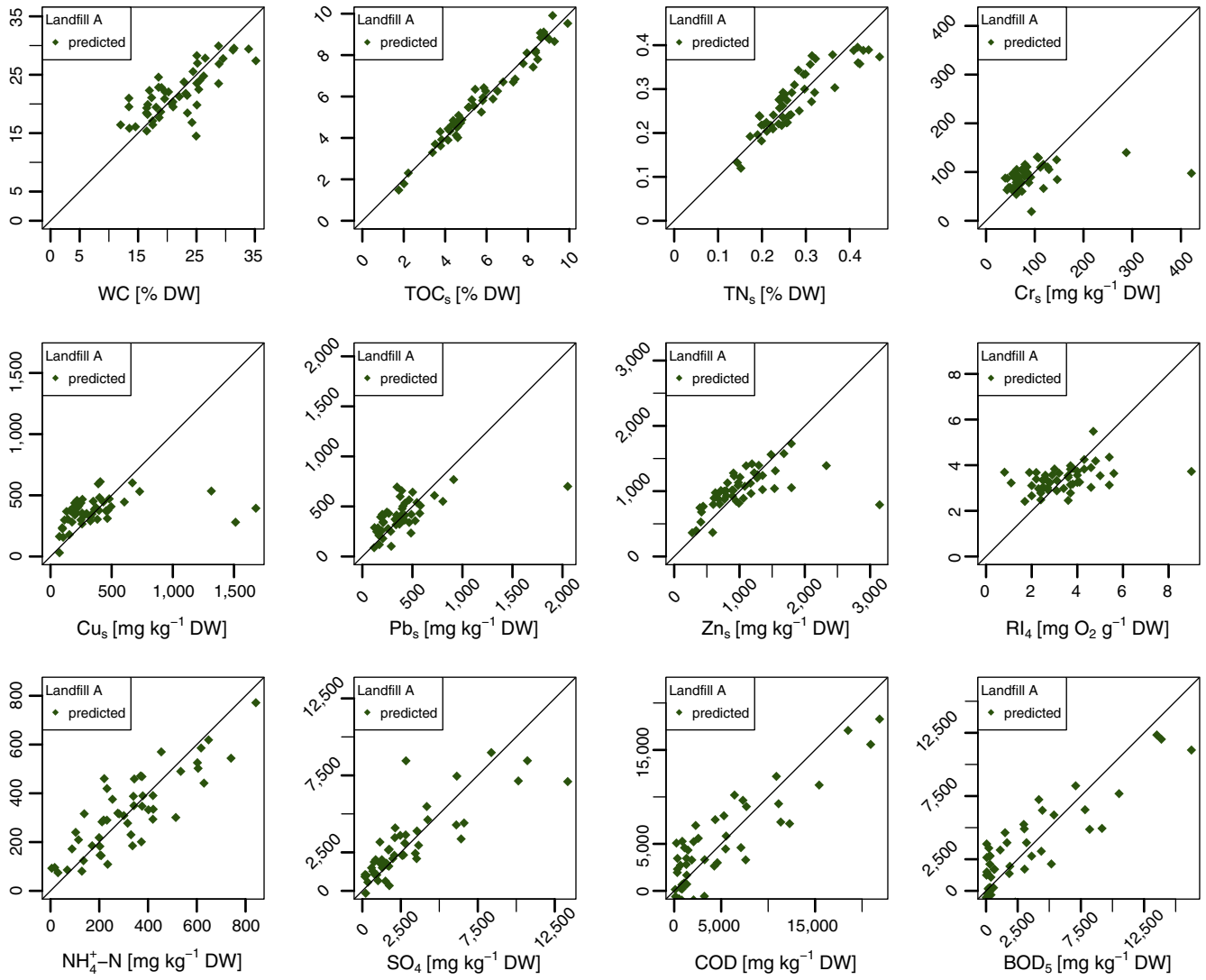

Fig. 3. Model creation for Landfill A (comparison between predicted and measured values of 12 variables). *Notes:* The *x*-axes can be considered as the measured values and the respective *y*-axes as predicted. The subscripted suffix s stands for solid. BOD_5, biological oxygen demand after 5 days; COD, chemical oxygen demand; DW, dry weight; TOC, total organic carbon; WC, water content.

3.4. Bootstrapping

The results of the RMdSPE bootstrapping were summarized in Fig. 4. The applied model adjustment criterion (less than 10% deviation from the adjustment with all data) was reached for WC, TOC_s, Pb_s and Zn_s as well as the eluate variables by using only few full measurements. This means, that <=ten variables for which the response variables are known as well, are needed for adjustment.

Fulfilling the criterion for Cr_s needed 11 observations (including the response variable) and TN_s, Cu_s and RI_4 needed more than 20 values (representing the whole plausible data set of Landfill B).

3.5. Application of the calibrated model (n = 10)

The results when adjusting the response variables with linear regression of ten observations (representing ten waste samples for which all response variables are known) and ten predicted values (subsequently named testing model) are shown in Fig. 5 and Table 3 (adjusted). Even though the bootstrapping test indicated that in many cases more than ten response variables would be needed to gain a reasonably good fit, the testing model was more accurate for most variables in comparison to the non-adjusted model. Only for SO_4 it was less accurate. This result is based on one random sample of ten response variables distributed over the whole dataset. For the bootstrapping procedure all observations were potentially considered, including extreme values. Most variables were predicted quite accurately with the RMdSPE below 30%, except for Pb_s, Zn_s, RI_4 and SO_4.

4. Discussion

4.1. Overall model quality

From the twelve predicted response variables, ten showed an RMdSPE below 35% (Model evaluation criterion), only for two (SO_4 and Zn_s) the accuracy was low (see Table 3 and Fig. 5). It has to be noted, that this criterion is based on the median, which is more robust to outlying values. The adjusting was performed by usage of ten observations out of 36, or 28% of all samples. If this number of required observations is specific for the present case (for Landfill A and Landfill B) or generally sufficient should be subject to further testing.

The variable SO_4 showed high variation for both landfills (Fig. 2), while in Landfill A this variable was probably stronger

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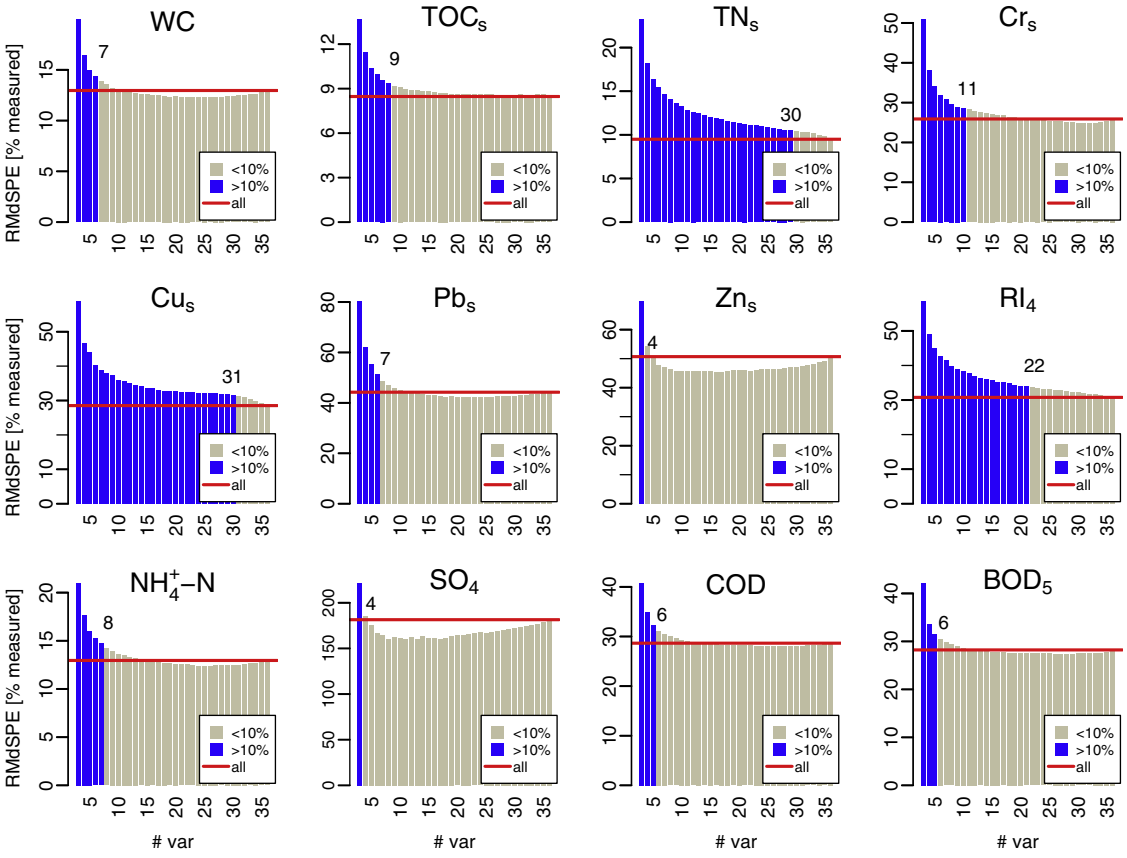

Fig. 4. Bootstrapping of the model results with a reduced amount of samples (RMdSPE). *Notes:* The red line represents the mean RMdSPE (root median square percentage error) of the model adjusted with all ($n = 36$) response variables. The figures above the bars indicate the amount of measurements to fulfill the 10% model adjustment criterion. The subscripted suffix s stands for solid. BOD_5, biological oxygen demand after 5 days; COD, chemical oxygen demand; RI_4, respiration index after 4 days; TOC, total organic carbon; WC, water content. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

influenced by construction and demolition waste, presumably containing gypsum, than in Landfill B. This could explain why the prediction for SO_4 was not as accurate as for other variables. Although the model did not predict some extremely high values correctly for the metal content and RI_4, the adjusted results for most of the variables were reasonably accurate. For assessing the spatial distribution of different variables inside landfills, it would be of higher significance to possess viable approximate values than fewer correct values. As an example, if we could assess the distribution of Cu_s showing a range from (38 to 804 mg kg^{-1} DW) in Landfill B with 26.1% (RMdSPE) accuracy after adjustment with higher sampling resolution, the information increase of the relative distribution would more than outweigh the inaccuracy of the model prediction.

The model should be applied for MSW-landfills only, since the calibration was performed for this landfill type. To increase the model accuracy especially for the underestimated higher values, the application of e.q. quadratic regression should be considered. Within the present article we introduced a linear model as a first step for the sake of applicability. Instead of our approach of adjusting the available model of Landfill A, it would also be possible to directly calculate the multivariate model for Landfill B by using as well ten measured values for calibration. But, as can be seen from Table 4, on average the result would be better with the presented model (lower RMdSPE). Moreover the variation of the outcome would be also lower (SD) for the majority of variables, proving that our presented approach would lead to more robust results. These results were as well derived with bootstrapping ($n = 5000$) without replacement for both models. We assume that by including the information of another dataset the variation of variables might be reduced. If the variation of a variable is high, showing e.g. many extreme values, the chance of sampling extreme values would rise as well. Directly calculating multilinear models based on these extreme values would possibly raise the variation in comparison to applying the model created on the basis of a whole additional dataset.

Another possibility would have been to calibrate the model for Landfill B and use the calibrated model to predict waste composition at Landfill A. This was accomplished (data not shown), however the model results were better in the presented way. Possible reasons for that might be that at Landfill A more samples were available for statistical modeling (50:36), the different landfill age (Landfill A is older and hence less affected by too pronounced relations), or also the sampling campaign focus might influence the model calibration.

4.2. Leachate loadings

Elution experiments target to simulate the potential leaching behavior of waste. With our model we addressed NH_4–N, SO_4, COD and BOD_5 as eluted response variables (unknown and hence to be predicted), while EC, pH and Cl were considered as eluted predictor variables (known). For the model of Landfill A, all four response variables (NH_4–N, SO_4, COD and BOD_5) could be predicted quite well. The lowest agreement between measured and predicted values has been observed for SO_4 with an r^2 of 0.66 (Table 4). The prediction of Landfill B was less successful, especially for SO_4, as already described under general model quality (see 4.1). The

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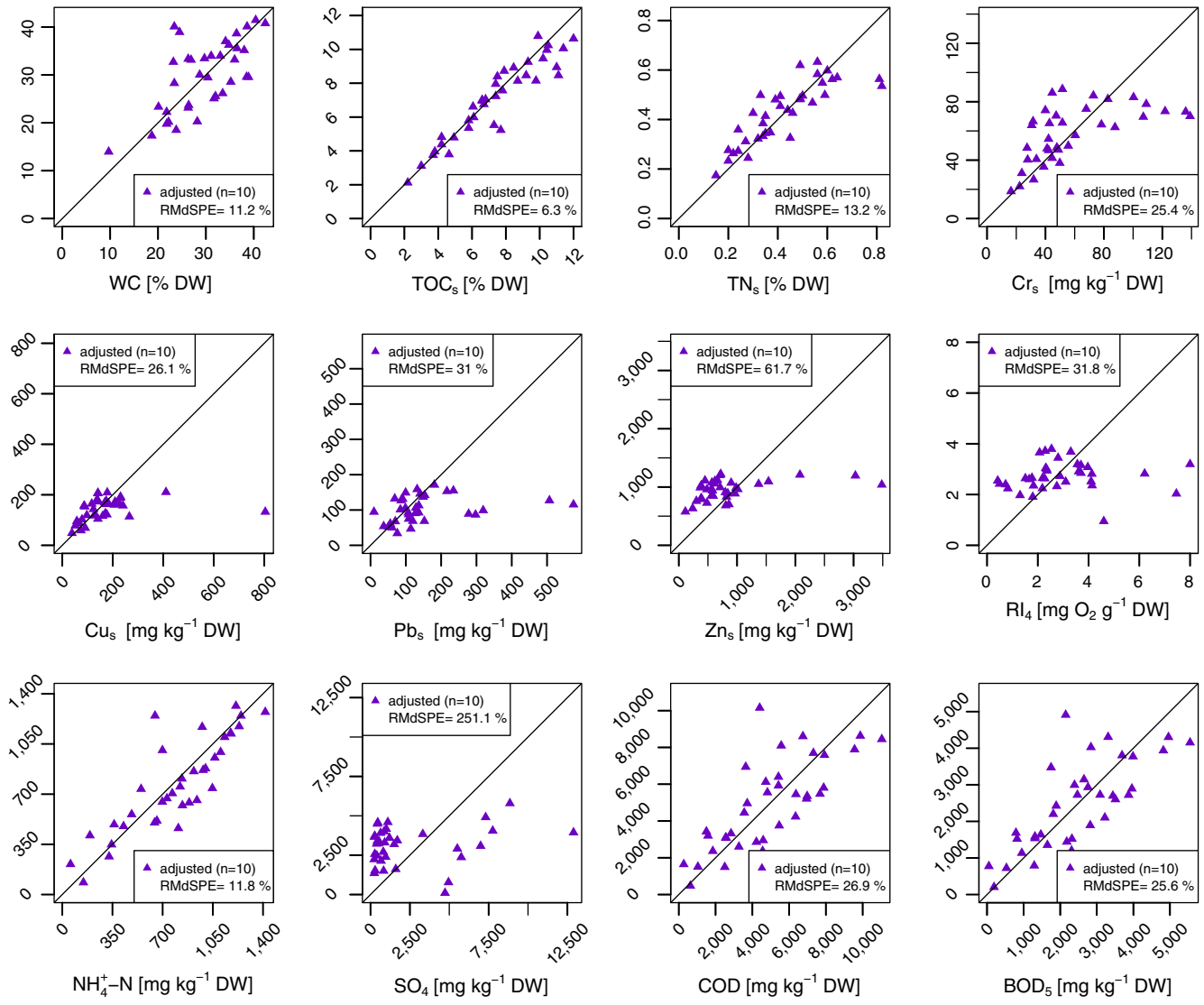

Fig. 5. Model testing via adjustment function derived from 10 random samples. *Notes:* The *x*-axes show the same range as the respective *y*-axes. The subscripted suffix s stands for solid. BOD_5, biological oxygen demand after 5 days; COD, chemical oxygen demand; DW, dry weight; RI_4, respiration index after 4 days; RMdSPE, root-median square percentage error; RMSPE, root-mean square percentage error; TOC, total organic carbon; WC, water content.

remaining elution response variables showed good (NH_4–N) to mediocre (COD, BOD_5) agreement (Table 3). After adjusting the results, the RMdSPE was below 30% for all the three variables. It has to be noted, that for COD and BOD_5 six predicted non-adjusted values were below zero and for SO_4 one, which became positive after the adjustment. For very low values of COD, BOD_5 and SO_4 the application of the model would possibly result in negative values, if the dataset has not been adjusted.

As discussed before, the tradeoff between measuring accuracy and frequency must be considered; applying our model to an increased amount of solid waste samples for which only four variables would have to be analyzed (higher measuring frequency with lower analytical extent) would result in an increased knowledge about the spatial distribution, while decreasing the measurement accuracy. This would certainly pose a disadvantage for values in the range of legal threshold values, but on the other hand improve the precision of the spatial distribution inside the landfill, which would be of higher importance for applying target-orientated mitigation measures, especially in large landfills. Finally, for assessing leachate migration preferential pathways inside the landfill (Laner et al., 2011) and the flow direction of the leachate plume still would need to be assessed. Without knowledge of the groundwater flow and the subsurface geology as it is often the case, solid waste sampling at landfills prevails the only method for assessing future emission potentials. With spatial knowledge about the potential leachate loadings, at least the emission source could be better characterized. The presented tool might help identifying these sources and thus facilitating such sampling campaigns.

4.3. Substance inventory

The prediction of the solid contents for Landfill A was mostly based on Loi and partly also on EC (WC and TN_s, Table 2). There was no significant explanation for Cr_s and Cu_s to be found at a 95% confidence interval. Still the RMdSPE of the adjusted model of Landfill B was below 35% for all solid variables except for Zn_s (RMdSPE 61.7%). As can be seen from Fig. 2, selected measured values of Cu_s, Pb_s and Zn_s in Landfill B were extraordinarily high in comparison to the remaining values, which was also the case in Landfill A. These few values were estimated far too low (Fig. 5). Generally, the applicability of the model was better for lower values, than for very high values. The upper limits for metal

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Table 4
Comparison between the adjusted model and a directly applied multivariate model.

Bootstrap n = 5000	Presented model with scaling RMdSPE (% measured)		Direct application on Landfill B RMdSPE (% measured)	
	Mean	SD	Mean	SD
Solids				
WC	13.0	2.37	13.9	3.49
TOC_s	9.11	2.20	10.8	3.05
TN_s	13.2	2.67	16.3	4.59
Cr_s	28.5	4.11	36.5	10.1
Cu_s	36.0	14.6	48.9	32.0
Pb_s	45.0	15.1	50.7	19.9
Zn_s	45.8	12.3	56.3	22.2
RI_4	38.2	9.7	30.4	12.2
Eluted				
NH_4–N	13.6	3.4	14.2	3.17
SO_4	162	83.6	162	72.9
COD	29.3	3.1	25.8	8.15
BOD_5	28.6	3.0	26.2	8.12

Notes: Both methods were performed based on 10 measured variables (5000 times). All numbers have been rounded to three significant figures. The subscripted suffix s stands for solid. BOD_5, biological oxygen demand; COD, chemical oxygen demand; DW, dry weight; EC, electrical conductivity; Loi, loss on ignition; LF, landfill; TN, total nitrogen; RI_4, respiration index after 4 days; RMdSPE, root-median square percentage error; TOC, total organic carbon.

concentrations according to the Austrian landfill ordinance are summarized in supplementary material (Appendix 3).

Besides the metallic contents, the TOC_s, the TN_s as well as the WC could be predicted quite accurately (RMdSPE < 15%). We could not predict the Fe_s-content for Landfill B as it was not measured there, but for Fe_s the r^2 of Landfill A would have been 0.64 (data not shown).

4.4. Summary of the model application

For an improved applicability of the model, a short application guideline is presented:

Step A – Solid waste sampling campaign performed.
Step B – Analysis of Loi, pH, EC and Cl for all samples taken.
Step C – Analysis of the response variables (that are to be predicted) at selected points (28%, or 10 out of 36 observations).
Step D – Application of model with measured variables (Step B) from Table 2 with units from Table 3 for each variable of interest.
Step E – Calculation of linear regression with the measured response variables (Step C) as predictor and the predictor variables from the same selection (28%, Step D) as response variables.
Step F – Adjustment of model output (Step D) with coefficients (distance + slope) from Step E.

The applied and adjusted model allowed for a reliable prediction for most of the examined response variables. It could be clearly shown, that for a good prediction it would not be necessary to measure every value during a sampling campaign. Especially for larger sites the presented tool could be useful for gaining an improved picture about the distribution of different substances in a landfill body with less analytical effort. There are two ways of future development of this tool: first it should be tested with solid waste data from other landfills in order to evaluate the number of variables required to perform reliable predictions of chemical waste characteristics. A second way would be to establish different multivariate linear regression coefficients for different types of landfills, to generally improve the prediction. For this second way, we strongly encourage establishing a database for landfill solid sampling data for improved statistical analysis and thus more accurate model prediction.

4.5. Landfill gas production

Present models predicting gas emissions are generally based on the content of degradable organic carbon (Kamalan et al., 2011). The TOC_s in Landfill A could be easily replaced by Loi (r^2 = 0.97, Table 3), which is simpler and cheaper to analyze, especially as also the prediction of TOC_s for Landfill B using Loi was of high accuracy (6.3% RMdSPE after adjustment). It has already been discussed by e.g. Prantl (2007) that in older MSW samples the correlation between TOC_s and the potential for landfill gas production diminishes. With the developed model, the RI_4 could only be predicted with low accuracy, since none of the underlying predictor variables significantly influenced the model result for the variable RI_4 (Table 2).

5. Conclusions

The application of the presented model would facilitate landfill sampling campaigns by reducing analytical efforts. In the prevailing case, a model adjustment on base of ten measured values (28%) led to quite accurate prediction values (<35% RMdSPE) for the majority of the observed variables.

In combination with higher sampling resolution, better spatial information concerning future emission potentials could be generated with the drawback of accuracy loss. Especially for bigger landfills without available waste inventories and a lack of information concerning groundwater flow and subsurface geology this screening tool could lead to an increased source understanding at reduced analytical costs.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.wasman.2014.08.009.

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