Supporting Information

Emissions of inorganic and organic arsenic compounds via the leachate pathway from pre-treated municipal waste materials - a landfill reactor study

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Waste materials

The mechanical-biological pre-treated municipal solid waste (MBP-MSW) material underwent a 4month rotting period in the dome aeration process. The dome aeration technology (DAT) developed by Paar and Brummack (2000) is a biological-mechanical treatment of residual waste and is applied to enhance the efficiency of the aerobic postmaturation of solid waste material (Paar et al., 1999). Aside waste incineration, the dome aeration technology represents one alternative way to process MSW, containing bio-degradable components, as required by the German legislation on the pretreatment of MSW prior to landfilling, which became obligatory in 2005 (Technische Anleitung Siedlungsabfall, TASi 1993, clause 12.1)

The waste material used in this study was sampled from a waste disposal site, which uses the dome aeration technology to reduce waste mass and volume, and to diminish the waste reactivity in terms of landfill gas emission, leachate pollution and settlement processes within the landfill body. The initial waste material was composed of 50 % municipal solid waste and 50 % bulky waste predominantly containing wooden debris as structuring element.

To provide a minimum amount of substrate homogeneity in all 6 reactors, the waste material was shredded to obtain a fraction <40 mm and subsequently homogenized. This material is characterised by an incineration loss of 50.8%, a TKN (total Kjehldal nitrogen) content of 15.5%, and furthermore by a high TOC content of 23.5%, pointing to a high reactivity potential, which is, according to the German legislation above the assignment value of 18% for mechanical-biological pre-treated municipal waste (AbfAblV, 2001).

Speciation of arsenic species and further analysis

Arsenate (As^V) and arsenite (As^{III}) were obtained as standard solutions (1.0 g L⁻¹) from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland). Monomethylarsonic acid (MMA), trimethylarsine oxide (TMAO), tetramethylarsonium oxide (TETRA) and arsenocholine (AsC) with purity \geq 97% were purchased from Argus Chemicals (Vernio, Italy). Arsenobetaine (AsB) (>95%) was obtained from Fluka. Dimethylarsinic acid (DMA) (\geq 97%) were gained from Merck. Deionized water, used throughout the work, was purified in a Milli-Q system (Milford, MA, USA). Individual stock solutions (50 mg As L⁻¹) of As^{III}, As^V, MMA, DMA, TMAO, TETRA, AsB and AsC were prepared in deionised water and stored at 4°C in the dark. A multi-species working solution of As^{III}, As^V, MMA and DMA with a total concentration of 10, 20 or 40 µg As L⁻¹ was prepared before each use by diluting the stock solutions with deionised water.

A high performance liquid chromatograph (HPLC) instrument (BIOTEK Instruments, USA), consisting of a gradient pump (System 525), capillary PEEK tubing (0.25 mm i. d.) and a 200-µL injection loop (Stainless Steel), and a HPLC autosampler 465 (Kontron Instruments, Germany) was

connected to a ion-exchange column and coupled to an ICP-MS (Agilent 7500c, Japan), equipped with a concentric nebulizer (Glass Expansion, Australia) and a Scott-type glass spray chamber.

The chemical analysis of the unfiltered leachate encompassed the measurement of the redoxpotential by electrode (Typ Mettler Toledo Pt 4805-S7/120), the pH by glass electrode (WTW, Typ Sen Tix 41), TOC (total organic C) by thermal oxidation to CO₂ (Shimadzu, TOC 5000 A). For chemical analysis of dissolved substances, leachates were 0.2 μ m membrane-filtered (Sartorius cellulose-acetate membrane filters). Dissolved organic carbon (DOC) was determined by thermal oxidation as CO₂ (Shimadzu, TOC 5000 A), COD (chemical oxygen demand) photometrically by cell test (Merck, Cell test 14555), NH₄-N (ammonia-N) and TKN (total Kjeldahl-N) by alkaline distillation and digestion, respectively, and back titration (Büchi systems, 736 GP Titrino METROHM). Anions (SO₄²⁻, NO₃⁻, Cl⁻) were detected by ion chromatography (Dionex). The proportion of particulate organic carbon (POC) in TOC was calculated by difference between TOC and DOC.

To determine total concentration of As and other elements in leachates, including both dissolved and particle phases, all leachates were digested with UV after addition of HNO_3 and H_2O_2 . The digested leachates were then measured with ICP-OES (Vista-Pro radial, Varian, Germany) and ICP-MS (Agilent 7500c, Japan).

Dome aeration process

The dome aeration technology (DAT) developed by Paar and Brummack (2000) is a biologicalmechanical treatment of residual waste and is applied to enhance the effectiveness of the aerobic postmaturation of solid waste material (Paar et al., 1999). Aside waste incineration, the DAT pretreatment of MSW represents one alternative way to process MSW, containing bio-degradable components, as required by the German legislation on the pre-treatment of MSW prior to landfilling, which became obligatory in 2005 (Technische Anleitung Siedlungsabfall, TASi 1993, clause 12.1).

Additional information about set up of "gas-tight" landfill reactors

With regard to gas exchange, the reactors of the anoxic treatments were closed systems, where the lid area on top of the reactors and the tube connectors were gas-tight sealed with silicone to avoid re-aeration or unrecorded gas losses, respectively (Fig. S5). The emitted gas was collected by polyethylene bags. In the oxic treatment, air was supplied to the reactors with flow rates of about 17.5 L air per hour (420 L of air per day). Here, the purged gas was run through a condensation trap in order to separate the water from the saturated air. The collected water was returned to the reactor. This method was used to avoid an uncontrolled loss of water from the system. For leachate

sampling, encompassing all reactors, the water volume sampled (2 liters) was completely replaced by tap water.

Quality assurance and control

Our Laboratory participates in a number of sample exchanges and certification programs for all analyzed parameters, including Germany Chemistry Society Exchange for foodstuffs, Bavarian State Agency of Water Economy Testing Program for sewage and waste water, Hessian State Agency of Environment and Geology for groundwater and raw water, Institut of Hygiene and Environment Testing Program for drinking water, University of Stuttgart, quality assurance/control of Baden Württemberg Testing Program for drinking, ground, sewage and waste water and Hamburg Environment Protection Agency Testing Program for sewage and waste water. The analyses of ignition loss, TOC, and TKN were performed according to the standard methods DIN EN 12879 (2001), DIN ISO 10694, and DIN EN 13342 (2001), respectively, were used.

Arsenic blank values in tap water

Total As concentration in tap water was 0.3 μ g As L⁻¹. The only As species presented was As^V.

Arsenic speciation

The quality control of our As speciation method was done with certificated standard DORM-2 with $16.7 \pm 0.8 \ \mu g \ g^{-1}$ and $0.22 \pm 0.07 \ \mu g \ g^{-1}$ of methanol-water extractable AsB and TETRA found (102% and 89% of certificated values, respectively). The analyzed values of As^{III}, As^V, MMA and DMA in DORM-2 have been provided in Huang and Ilgen (2008). However, no certificated values of these As species were provided. Additionally, the laboratory participated in the sample exchange and certification programs from Germany Chemistry Society (GDCh) for As speciation with satisfactory results (see http://www.gdch.de/strukturen/fg/lm/ag/anorg/arsen.htm).

Total arsenic determination in solid phases

Analysis of Astotal based on HNO₃-HCl digestion has been applied to different certificated solid phases with recoveries ranged between 90–110%. Our certificated materials include lake sediments (LKSD-1, LKSD-2, LKSD-3, LKSD-4, Geological Survey of Canada), Tibet soil NCS DC 78302 (China National Analysis Center for Iron and Steel, 1997), CRM 7003 and CRM 7004 silty clay loam with normal or rather elevated analyte levels (Czech Metrological Institute, Brno, 1995), GBW 07605 tea (Institute of Geophysical and Geochemical Exploration, Langfang, China, 1990), leaves of poplar (China National Analysis Center for Iron and Steel, Beijing, 2004), Materials 2008), plankton (Institute for Reference and Measurements, Belgium,

CTA-VTL-2, tobacco leaves (Institute of Nuclear Chemistry and Technology, Poland, 1997) and pine needles, SRM 1575 (NBS, 1976).

Quality control of As_{total} determination in solid phases was also conducted by comparing the results from HNO₃-HCl digestion and X-ray fluorescence spectrometry (XRF) (Table 1S). For XRF analysis, 4.0 g of soil powder were mixed with 0.9 g of Licowax® C Micropowder PM (Clariant, Switzerland), pressed into a 32-mm pellet and analyzed using an energy dispersive X-ray fluorescence spectrometer (SPECTRO X-LAB 2000, SPECTRO Analytical Instruments, Germany). The validation of HNO₃-HCl method was supported by little difference between the As_{total} concentrations based on HNO₃-HCl method and XRF in soils with largely different characteristics (e.g. C% ranged 5.2–49.2).

Summarized discussion of leachate quality parameters

Under oxic conditions, leachate pH values increased rapidly from 7 to 8 during the first 10 weeks and leveled off to 8.5 (Fig. S2). Comparably, the pH values in the anoxic reactors kept constant at 7. Due to the activity of hydrolytic, fermentative and acetogenic bacteria and methanogens, the pH in anoxic treatments was approximately neutral over a relative narrow range. The electrical conductivity and the concentrations of total (organic and inorganic) C, TKN, Cl⁻, Na⁺, K⁺, Mg²⁺ and most trace elements in leachates decreased with time in all reactors, suggesting a fast decomposition of MBP-MSW at the beginning of incubations or wash out/ dilution effects. The general high release rates of elements and compounds during the early stage of incubation might be due to different processes. First, the preparation of the waste material (sieving to 40 mm) and its installation into the reactors may cause the disruption and disturbance of material aggregates resulting in enhanced surface areas and hence new accessibility to leachable element deposits. Second, the favorable conditions during the initial short oxic phase might promote microbial aerobic degradation and mineralization processes, which result in higher mobilization rates of organically-originating compounds such as TOC and TKN. However, an accurate assessment of the contribution of single processes to the overall release is not possible here. The occurrence of NH₄⁺, NO3⁻, S, SO4²⁻, Fe and Mn in leachates well reflected the redox conditions in the reactors established by the different treatments: Ammonium was the predominant N species under anoxic conditions. The concentrations of Fe and Mn in leachates were in the order: in anoxic reactors with underlying soils > anoxic >> oxic reactors. The higher Fe and Mn concentrations in anoxic than oxic leachates revealed the occurrence of reductive dissolution of Fe and Mn (hydr)oxides under anoxic conditions. Much higher concentrations of Fe and Mn in leachates in anoxic set-up with underlying soils were due to the additional contribution of Fe and Mn (hydr)oxide dissolution from underlying soils. Dissolved S was only detectable in oxic leachates with concentrations

approaching 2000 mg L⁻¹ and was likely presented mostly as SO₄^{2–}. According to Eh-pH diagram, dissolved sulphides are relative unstable under the neutral and basic conditions here than acidic conditions. High metal concentrations may suppress the dissolved sulphide by precipitation. The annual releases of Cd, Cu, Ni, U and Zn via leachates were higher in the oxic than in anoxic treatments (Table S1). This finding reflects the capability of sulphides to form precipitates with Cd, Ni, Zn and Cu. In contrast, more Ba, Co, Cr, Se and Sn were released under anoxic than oxic conditions.

Artefact of arsenic speciation

Transformation of methylated arsenic^{III} and thioarsenic species during storage

Methylated As^{III} and thioarsenic species may undergo oxidation to their respective As oxyanions or loss of thio-structural moieties in exposure with oxygen during storage. Gong et al. (2001) indicated that monomethylarsonous acid (MMA^{III}) and dimethylarsinous acid (DMA^{III}) are much less stable than other (methylated) As oxyanions. Their stability is matrix and temperature dependent. About 15% of spiked MMA^{III} transferred to MMA in de-ionized water at pH 6.0 in 3 days. Decreasing the storage temperature to 4 or -20° C, MMA^{III} may keep stable up to 4 months. However, most MMA^{III} in urine was oxidized over 5 months under 4 and -20° C storage. Dimethylarsinous acid water at 4 and -20° C.

In comparison, the oxidation of methylated thioarsenic species to the respective As oxyanions were generally slow at wide ranges of pH (3.0, 8.0 and 10, Conklin et al., 2008). The stability of methylated thioarsenic species decreased only slightly with decreasing pH values. The sample storage temperature affected the stability methylated thioarsenic species more than pH. Although the spiked samples were best preserved at 4°C for 7 weeks, the difference between 4 and 25°C was no more than 1% weekly. However, the sulphide to oxide transformation was largely accelerated at 60°C (Conklin et al., 2008). The past data suggested that the oxidation half-life of methylated thioarsenic species at 4°C may be on the order of one month (Wallschläger and London, 2008).

Opposite to oxidation of thioarsenic species, thioarsenic species may form in solutions containing both sulphide and As oxyanions. Transformation of methylated As^{V} species to corresponding sulphide species is a function of pH and sulphide concentrations (Conklin et al., 2008). Conversion of methylated As^{V} to the sulphide form was generally little above pH 8.0, while such conversion was observed below pH 7.0. The basic condition benefits the preservation of methylated As^{V} where sulphide was most presented as HS⁻. It is suggested that H₂S may need to be present for oxygen/sulphur exchange to occur, as opposed to HS⁻ (pK_a= 7). The conversion of

TMAO to trimethylarsine sulphide required less sulphide concentrations than DMA and MMA. The stability of thioarsenic species is also pH and temperature dependent (Conklin et al., 2008).

Transformation of methylated As^V to corresponding sulphides in oxic landfill simulators was little due to the slightly basic condition (pH >8.0) over the period of incubation (Fig. S1). In comparison, the pH values slightly higher than 7.0 may allow certain extents of methylated As^V converting to sulphides in anoxic landfill simulators. Still, such transformation is estimated little due to low concentrations of dissolved sulphide (Fig. S6). In addition, conversion of oxide to sulphide seems to reach equilibrium at the moment of sampling. An exposure of oxygen may conversely drive the transformation of thioarsenic species to As oxyanions and sulphide to sulphate. The oxidation of thioarsenic species was relatively slow (Conklin et al., 2008; Wallschläger and London, 2008). Additionally, the neutral to slightly basic pH values of leachates prevented from either transformation of thioarsenate species into As oxyanions (Stauder et al., 2005) or precipitation of As-sulphide minerals (Wallschläger and Stadey, 2007) during the storage less than 48 hours. Methylated As^{III} species, especially DMA^{III}, may be quite unstable in leachates due to the complicated matrix during storage. However, low temperature condition (4°C) seem to be the best way to improve the stability of As species, especially methylated As^{III}, without further interference on As speciation, e.g. $As_2S_{3(s)}$ precipitation by acidification. Rapid analysis (within 48 hours) may help to reveal the true As speciation mostly.

Freeze drying

Freeze drying was taken as a necessary pre-treatment procedure for MBP-MSW for a better homogenization of samples consisted of different materials in various sizes e.g. MBP-MSW, even freeze drying has been demonstrated to be able to change As speciation (Huang and Ilgen, 2006). Especially the samples rich in organic substances may have larger shift of As speciation than the mineral samples. This is probably due to loss of water extractable As during drying (Huang and Ilgen, 2004), which took many days since organic samples contain usually high amounts of water. On the other hand, drying may result in a change of the sample composition or redistribution of As species into other phases, which immobilize parts of the extractable As, especially inorganic As, from the samples. Krachler and Emons (2000) suggested that extraction yields for freeze-drying and may lead to the formation of agglomerates that hamper the extraction of the analyte. Rapin et al. (1986) suggested that some minerals become more crystalline during the freeze-drying. We extract our MSW solid materials and underlying soils for As speciation with concentrated phosphoric acid. Thus, such artefacts were estimated to be relatively low. This is because that the extraction recovery based on concentrated phosphoric acid (46-54% for oxic and 12% for anoxic

treated organic and mineral samples in this study) is much higher than that based on water or methanol-water (usually <5%). Additionally, the water content of MSW and underlying mineral soils are all low, so that the time required for drying was short. Loss of As species during drying could be thus minimized. Arsenite may oxidize to As^{V} in contact with the atmospheric oxygen during drying. This took place more likely in the case of mineral soils. Conversely, reduction of As^{V} to As^{III} may be accompanied with the oxidation of the organic matters in samples rich in organic matters. In comparison, the variation in speciation of organic As was demonstrated less than that of the inorganic As (Huang and Ilgen, 2006). Accordingly, transformation of As^{III} and As^{V} in our samples, especially anoxic treated MPB-MSW, during drying seems to be inevitable. Since the extent of this transformation depends strongly on the nature of the organic samples (Huang and Ilgen, 2006), we are not able to estimate the extent of this artefact.

Sample dilution

Sample dilution was shown to change the species distribution between thioarsenic and arsenic oxyanions (Beak et al., 2008). Thioarsenic species was demonstrated to convert to As^{III} by dilution at pH 9.7 with a dissolved sulphide concentration of 0.3 mM. Since we conducted the As speciation in filtered leachates without dilution, there was no such artefact. How dilution affects the As speciation in 1 M H₃PO₄ extract after 100 times dilution is not able to know due to lacks of knowledge. However, the acidic condition seems to restrain this effect by precipitation of As-S species.

Limitation of chromatographic methods

The chromatographic methods used in this study may not separate and identify all known dissolved As species. The method based on PRP-X100 anion exchange using a phosphate buffer isocratically as a mobile phase is one of the most popular chromatographic methods for the separation of anionic As, As^{III}, As^V, MMA and DMA (Huang and Ilgen, 2008). However, this method may not be suitable for separation and identification of all As species. Conklin et al. (2008) took PRP-X100 column with 10 mM phosphate and nitrate buffers at pH 4.5 to monitor the interconversion between MMA and its sulphide analogues. For separating DMA, TMAO and their sulphide analogues, another chromatographic method based on C-18 column was taken. Methods based on PRP-X100 column was used for speciation of As-S species, however, mostly concerning with thioarsenosugars (Fricke et a., 2004; Nischwitz et al., 2006; Conklin et al., 2006; Sean et al., 2006).

The chromatographic method based on Zorbax 300-SCX cation exchange column is usually used for speciation of cationic As species, e.g. TMAO, TETRA, AsB and AsC (Francesconi et al., 2002). This method may not separate methylated As^{III} species due to their anionic nature. The acidic

mobile phase (pH 2.6) may lead to rapid decomposition of the As-S species or precipitation in the form of As-sulphide minerals (Wallschläger and Stadey, 2007).

Estimation of concentrations of dissolved sulphide

To our knowledge, there is little information available about the dissolved sulphide in landfill leachates. According to Eh-pH diagram, dissolved sulphides are relative unstable under the typical neutral and basic conditions in landfills than acidic conditions. High metal concentrations may suppress the dissolved sulphide by precipitation. The objective of calculating dissolved sulphide concentrations is to understand the speciation of dissolved S in leachates and its consequent influence on the transformation and mobility of As. The most popular 'methylene blue method' determine dissolved sulphide species including H_2S , HS^- and S^{2-} (Cline et al., 1969). Thus, we took the sum of dissolved H_2S , HS^- and S^{2-} as dissolved sulphide concentrations.

We first calculated the thermodynamically allowed concentrations of dissolved sulphides according to the measured pH, redox potentials and total S concentrations as follows:

$$\frac{1}{8}SO_{4}^{2-} + \frac{9}{8}H^{+} + e^{-} \implies \frac{1}{8}HS^{-} + \frac{1}{2}H_{2}O$$
pE° = 4.25
use Nernst equation: pE = pE° + log $\frac{[H^{+}]^{\frac{9}{8}}[SO_{4}^{2-}]^{\frac{1}{8}}}{[HS^{-}]^{\frac{1}{8}}}$
after rearrangement pE = pE° - $\frac{9}{8}pH + \frac{1}{8}log \frac{[SO_{4}^{2-}]}{[HS^{-}]}$

This equation was taken for calculation of the ratio of SO_4^{2-} to HS⁻ with the measured pH and redox potentials. The concentrations of sulphide and sulphate can be thus obtained together with the following 2 equations.

$$[\text{Total S}] = [S^{2^{-}}]_{\text{total}} + [SO_{4}^{2^{-}}]_{\text{total}}$$

$$[\text{HS}^{-}] = \frac{[S^{2^{-}}]_{\text{total}}}{(1 + \frac{[\text{H}^{+}]}{\text{K}_{a1}} + \frac{\text{K}_{a2}}{[\text{H}^{+}]})} \text{ and } [SO_{4}^{2^{-}}] = \frac{[SO_{4}^{2^{-}}]_{\text{total}}}{(1 + \frac{[\text{H}^{+}]}{\text{K}_{a}})} \text{ , whereas } pK_{a1} = 7.0 \text{ and } pK_{a2} = 12.9 \text{ for}$$

 H_2S and $pK_a=1.9$ for HSO_4^- .

We estimated parallel the concentrations of dissolved sulphides based on the measured concentrations of heavy metals and the solubility constants (K_{sp}) of the respective metal-sulphide precipitates in Skoog et al. (1992) (Fig. S6). This helps to check the dissolved sulphide concentrations from the aspect of solubility, although the true concentrations may be determined by

another factors e.g. pH and redox potentials. Additionally, the measured heavy metal concentrations may represent not only the species for solubility calculation (e.g. Cu^{2+} for CuS calculation) but also other species (Cu⁺, Cu⁰, and colloidal bounded Cu). The calculation of sulphide from $MS_{(s)} \iff M^{2+} + S^{2-}$ was based on the following equations:

$$K_{sp} = [M^{2+}][S^{2-}]$$

Whereas we supposed the $[M^{2+}]$ was equal to the ICP-MS/ ICP-OES determined concentrations.

$$[S^{2-}]_{\text{total}} = [H_2S] + [HS^{-}] + [S^{2-}] = \frac{[H^+]}{K_{a1}} \cdot \frac{[H^+][S^{2-}]}{K_{a2}} + \frac{[H^+][S^{2-}]}{K_{a2}} + [S^{2-}]$$

For both calculations, we hypothesized that the kinetics of redox transformation of sulphate and sulphide, metal sulphide precipitation and dissociation of H_2S and HSO_4^- are so rapid that their thermodynamic equilibrium was little influenced by reaction kinetics. This is especially true when we monitored the concentrations in an interval of 14 days. These estimations are not able to provide exact concentrations of dissolved sulphide. However, it allows us to gain an insight into the potential concentrations range of dissolved sulphide in our leachates.

The results of calculation based on Eh and pH indicate the absence and trace amounts of sulphide $(10^{-4} \sim 10^{-15} \text{ mg S L}^{-1})$ in oxic and anoxic leachates, respectively (Fig. S6). This coincides well with no findings of dissolved sulphide, calculated from the difference between our measured total S and sulphate (Fig. S2). Still, concentrations of dissolved sulphide in anoxic leachates may allow to precipitate certain metals, as indicated by K_{sp} calculation. The solubility estimation suggests also very low concentrations of dissolved sulphide in all leachates allowed (< 10^{-3} and < 10^{-4} mg S L⁻¹ in oxic and anoxic leachates). The absence of dissolved sulphide in oxic leachates based on Eh-pH calculation hints the failed estimation with K_{sp} . This explains the higher concentrations of Zn, Cd, Ni and Cu in oxic than in anoxic leachates. Even though there is rapid oxidation of sulphide during storage, it represents only a tiny part of the true sulphate concentrations.

Gas composition in landfill simulators during incubation

The gas composition of the oxic and anoxic reactors in first 5 months differed significantly in the course of the study (Fig. S7). During the pre-treatment anaerobic phase, both the oxic and the anoxic treatments showed similar values with regard to the emitted gas volume and composition exhibiting emission volumes of about 150 liters during the first 2 weeks and CO_2 , CH_4 and N_2 proportions of 65, 20 and 12%, respectively. However, with the aeration of the oxic treatment, methane production declined immediately towards zero, whereas CO_2 and N_2 proportions yielded to approximately 10 and 80%, respectively, for the rest of the study period. From week 12 onwards

the anoxic treatments showed stable gas composition of about 40% CO₂, 55% CH₄ and <3% N₂ and constant fortnightly gas volumes of 30 to 40 liters.

Unknown peaks in Fig. 1b.

The retention time of 2 unknown peaks in Fig. 1b is near to the position of dead volume. The peak with retention time of 1.5 minutes (?1) represented a mixture of As^{III}, As^V, MMA and DMA in oxic leachates (Fig. S8a). These neutral and anionic As species interact little with the stationary phase of cation exchange column and exhibit thus little retention. The peak with retention time of 1.7 minutes (?2) originated from mixed standards of AsB, AsC, TMAO and TETRA. The real cause of this artefact peak is not clear (Fig. S8b).

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	Forest floor (Oi)	Forest floor (Oe)	Forest floor (Oa)	Wetland soil	Bhs horizon
As (ppm) HNO3-HCl digestion	2.3	12.9	17.9	2.9	16.3
As (ppm) _{XRF}	2.3	14.7	18.3	2.8	17.1
Depth (cm)	7-6	6-3.5	3.5-0	50-60	9–20
$pH_{\left(H_{2}O\right) }$	5.7	5.8	4.0	4.8	4.6
C (%)	49.2	34.8	20.3	7.5	5.2
Si (%)	1.9	7.7	5.0	22.3	20.5
Al (%)	0.28	1.8	1.1	5.7	7.0
Fe (%)	0.16	1.0	0.65	1.1	3.8
Mn (ppm)	222	153	53	167	314
S (ppm)	1451	2780	2600	652	487

Table S1. Carbon contents and pH, total Si, Al, Fe, Mn, S and As concentrations of the investigated soils

Treatment	Ba	Cd	Со	Cr	Cu	Ni	Pb	Se	Sb	Sn	Sr	U	Zn
Oxic treatment 1	155	5.43	8.77	94.6	276	131	3.51	1.28	21.1	6.28	2570	0.92	1160
Oxic treatment 2	140	3.76	6.19	91.3	285	113	4.38	1.18	19.8	4.94	2200	0.66	809
Anoxic treatment 1	778	0.07	22.8	212	5.91	93.6	1.93	1.72	14.8	40.6	1190	0	31
Anoxic treatment 2	1140	0.15	24.1	228	6.23	99.1	3.68	1.81	15.2	41.1	1360	0	39
Anoxic treatment + soil 1	951	0.31	25.3	156	12.3	92.3	3.87	1.82	12.6	21.8	1450	0.22	38
Anoxic treatment + soil 2	927	0.59	28.8	200	16.0	97.0	9.89	2.38	13.6	21.3	1530	0.48	102

Table S2. Cumulative amounts of heavy elements (mg kg⁻¹ yr⁻¹) released via the leachate pathway over one year.



Figure S1. Concentrations of organic arsenic species (in logarithmic scale) in the leachates from MBP-MSW in the oxic, anoxic and anoxic + underlying soil landfill reactors over one year incubations. MMA: monomethylarsonic acid, DMA: dimethylarsinic acid, TMAO: trimethylarsine oxide, TETRA: tetramethylarsonium ion and AsB: arsenobetaine. Mean values of 2 experimental replicates are shown. The missing points represented values below the detection limit (0.01 μ g As L⁻¹).









Figure S2. pH values, conductivities, redox potentials and concentrations of O_2 , Na, K, Mg, Ca, B, Fe, Mn, Al, Si, SO_4^{2-} , NO_3^{-} , NH_4^+ -N, Cl⁻, total C and TKN in the leachate from mechanical-biological pre-treated municipal solid waste in the oxic, anoxic and anoxic + underlying soil landfill reactors.





Figure S3. Concentrations of heavy metals in the leachate from mechanical-biological pre-treated municipal solid waste in the oxic, anoxic and anoxic + underlying soil landfill reactors over one year incubation. Mean values of 2 experimental replicates are shown.



Figure S4. Concentrations of total arsenic in the UV-digested vs 0.2 μ m filtered leachate from mechanical-biological pre-treated municipal solid waste in the oxic, anoxic and anoxic + underlying soil landfill reactors. n = 54 for each treatment.



Figure S5. Landfill simulation reactor showing the experimental design of the a) anoxic + soil layer, b) oxic and c) anoxic MBP-MSW set-up (modified after Andreas, 2000)



Figure S6. Concentrations of total dissolved sulphide ($H_2S + HS^- + S^{2-}$) and sulphate ($HSO_4^- + SO_4^{2-}$) in mg S L⁻¹ in the leachate from mechanical-biological pre-treated municipal solid waste in the oxic, anoxic and anoxic + underlying soil landfill reactors over one year incubation. Eh & pH S2– and SO4: calculated concentrations of total dissolved sulphide and sulphate based on the measured total sulphur concentrations, pH and redox potentials. MnS, CoS, NiS, CuS, FeS, ZnS, PbS, SnS and CdS: Estimated based on the solubility of the corresponding sulphides.



Figure S7. Gas composition the oxic and anoxic reactors during the first five months.



Figure S8. Cation exchange chromatogram of 5 μ g As L⁻¹ of arsenic standards (a) and arsenic species in oxic leachates from mechanical-biological pre-treated municipal solid waste. AsB: arsenobetaine, TMAO: trimethylarsine oxide, AsC: arsenochorine, TETRA: tetramethylarsonium ion.