



Changing pH, organic matter, and redox state govern contaminant mobility during waste stabilization in landfill simulation reactors

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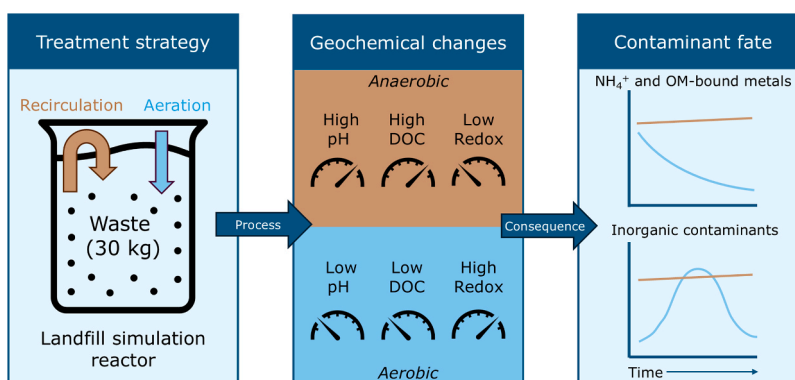
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HIGHLIGHTS

- Controlled reduction of contaminant leaching was investigated in waste reactors.
- Ammonium and organic-bound contaminants decreased under aerobic conditions.
- Specific contaminants first increased and then decreased under aeration.
- Geochemical modelling facilitated description of underlying mechanisms.
- Identified trade-offs in leaching risks require careful treatment strategies.

GRAPHICAL ABSTRACT



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ABSTRACT

Landfills remain an important endpoint for waste and waste residues, yet current management in the Netherlands requires eternal aftercare to protect public health and the environment. Enhanced waste stabilization in landfills through active treatment, i.e. aeration and leachate recirculation, has potential as a sustainable alternative to current landfill management. However, the influence of active treatment on solid waste properties and subsequent leaching of hazardous contaminants has only received limited investigation. This study investigates these influences in landfill simulation reactors containing 30 kg of waste from different origins, which were treated using aeration, leachate recirculation, and their combination. Large differences in leachate contaminant concentrations were found between treatments. A shift from leachate recirculation to aeration changed prevailing redox conditions from anaerobic to aerobic and decreased pH and dissolved organic and inorganic carbon. Consequently, concentrations of ammonium and inorganic contaminants with a high organic matter binding affinity decreased, whereas other inorganic contaminants first increased in concentration due to mineral dissolution followed by a decrease due to mineral precipitation or binding to reactive surfaces. The underlying mechanisms of these trends were identified based on geochemical modelling. The observed changes during aeration were accelerated when aeration was preceded by leachate recirculation, and concentrations rebounded when anaerobic conditions were reintroduced. Our findings ultimately demonstrate that active treatment of

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landfills requires careful consideration of the most effective strategy, as trade-offs in contaminant leaching mean their potential risks should be weighed against each other.

1. Introduction

A continuous increase in global waste generation [1,2] has led governments to explore sustainable alternatives to landfills for waste management [3–5]. Nevertheless, landfills remain a necessary waste endpoint due to the existence of untreatable waste and waste residues. Landfills are a source of hazardous emissions, posing a risk to public health and the environment through the generation of greenhouse gases, namely methane [6,7], and contaminant-rich leachate [8–10]. These emissions are prevented by encapsulating the waste in artificial barriers [11], yet this approach delays waste decomposition and retains the waste emission potential. As a result, the so-called “aftercare” period, i. e. the period following waste acceptance in which landfills are thoroughly monitored, can be lengthy and in certain cases indefinite, leading to high societal costs [12].

The need for more sustainable landfill management has led to the signing of a “green deal” between the Dutch government, landfill operators, and knowledge institutes [13]. This green deal initiated three landfill-scale pilot projects to assess the potential of aeration and leachate recirculation as active treatment for reducing contaminant emissions to comply with legally accepted emission target values (ETV) [13,14]. In conjunction with a large associated research programme, an extensive monitoring programme has been developed to quantify active treatment effects on gaseous and leachate emissions [15].

Assessing the true potential of long-term active treatment to reduce leachate contamination requires knowledge of both the changes in leachate contaminant concentrations, and on the geochemical evolution of the solid waste and its corresponding effects on contaminant transport. Studies of the latter are scarce, as *in situ* monitoring of solid waste is challenging and costly. Laboratory-scale alternatives for determining solid-phase changes are Landfill Simulation Reactors (LSRs), which provide the additional benefit of an accelerated stabilization rate compared with field treatment to give insights on shorter timescales [16, 17]. While LSRs are well established, previous research has primarily focused on gas production, chemical and biological oxygen demand, pH, nitrogen, carbon, and macro ions [18–26]. Crucially, existing studies on inorganic contaminants have largely overlooked the role of organic matter (OM) [27–31], a key factor governing the solid/solution partitioning of heavy metals [32–34]. Furthermore, studies investigating mechanisms underlying contaminant mobility, substantiated by mechanistic modelling, are scarce and have, to our knowledge, been limited to gas production and trends in pH and macro ions [35]. Consequently, the geochemical processes driving the leachability of inorganic contaminants during active treatment in LSRs remain underexplored.

To address this gap, geochemical mechanisms can be elucidated by coupling dedicated leaching experiments with “multi-surface” geochemical modelling. This modelling framework calculates chemical interactions – including binding to reactive surfaces, inorganic complexation, and mineral precipitation [36] – and thereby offers a comprehensive view of chemical speciation. These models have successfully identified underlying processes in batch extractions of landfill waste [37–39] and highlighted redox chemistry as an important *in situ* contaminant solubility-governing parameter in landfill pore-water [40], and thus are a promising tool for exploring contaminant partitioning in LSR studies.

This study investigates the mechanisms underlying ammonium (NH_4^+) and inorganic contaminant leaching from actively treated waste in LSRs. This was done by operating eight LSRs under distinct dynamic conditions: leachate recirculation under anaerobic conditions, aeration, and a combination of both. The LSRs were operated for 682 days, with frequent leachate sampling for the analyses of OM and contaminant

concentrations. A unique feature of this paper is that observed contaminant leaching trends from the dynamic LSRs were interpreted by a mechanistic geochemical model approach, originally developed to identify chemical release mechanisms in landfilled waste under batch conditions [39]. The model was parametrized using pH and *in situ* redox measurements, alongside reactive surface data derived from independent selective extractions. By coupling the long-term monitoring of over 20 inorganic contaminants with geochemical modelling to pinpoint specific solubility-controlling mechanisms, we provide a more comprehensive understanding of contaminant leaching compared with previous LSR studies. Furthermore, our findings reveal the complex trade-offs between contaminant leachability and the time required for effective treatment, providing essential data for validating active treatment as a sustainable landfill management strategy.

2. Materials and methods

2.1. Landfill solid waste sampling

Solid waste samples were collected from the three Dutch pilot landfills: Braambergen 11 N (Bra), containing contaminated soil, remediation residues, and construction and demolition (C&D) waste; Kragge (Kra), containing commercial, domestic, and C&D waste; and Wieringermeer (Wie), containing commercial waste, composting residues, and contaminated soils [41]. Sampling was conducted approximately five years after the initiation of active treatment at each site: September 2022 (Bra), October 2022 (Wie), and March 2023 (Kra).

The sampling strategy prioritized obtaining sufficient bulk volume for the LSR experiments (see Section 2.2) rather than establishing spatial representativeness of the pilot sites. Vertical drilling was performed using a sonic sample drill at multiple locations (Bra: 7; Kra: 11; Wie: 3). Drilling proceeded in two-meter intervals until an impenetrable layer or the basal drainage was reached (maximum depths: 12 m at Bra, 18 m at Kra, and 14 m at Wie).

To minimize preferential flow paths in the reactors, the collected waste was sieved to < 36 mm (<10% of the LSR inner diameter, to limit preferential flow [42]) and thoroughly homogenized prior to filling the LSRs. A subsample was dried at 105 °C to determine moisture content and characterized for parameters relevant for contaminant leaching (Section 2.3), and to evaluate the pH-dependent leaching of contaminants (Section SM2, SI).

2.2. Landfill simulation reactors

2.2.1. General set-up

A schematic overview of the LSRs is provided in Fig. 1. Briefly, the LSRs consisted of polypropylene (PP) cylinders (60 cm height, 38 cm diameter). A perforated disc (10 mm thickness, 10 mm pore size) separated the waste from the leachate reservoir. An aeration ring was positioned on top of this disc to introduce nitrogen or compressed air; to prevent clogging, this ring was sandwiched between layers of 1 mm PP mesh. Leachate was recirculated using an impeller pump (Modified F2P10–19, Johnson Pump, Sweden) and distributed evenly via a custom 3D-printed PP divider. All reactors were insulated with foam rubber and heated via mats to maintain an internal temperature of 34 °C.

The LSRs were filled with moist waste equivalent to 27 kg dry matter (DM) for Kra and 30 kg DM for Bra and Wie. Subsequently, 1 L of demineralized water was added to non-recirculation LSRs (final moisture content: Bra 38%, Kra 75%, Wie 41%). Recirculation LSRs required higher volumes of water to ensure pump functionality, with variable amounts added due to differing water retention capacities (added water:

Bra 9 L, Kra 5 L, Wie 8 L; final moisture contents: Bra 68%, Kra 90%, Wie 62%). Redox potential of the waste was logged hourly using an *in situ* redox probe (ORP 40-4-B, Swap Instruments, NL) and a separate reference electrode (Ag/AgCl, KCl, 3 M, REF-12-0-A, Swap Instruments, NL), at 7.5, 17.5, 27.5, and 37.5 cm (measured from the bottom of the waste). The redox potential was recalculated from mV to pe, correcting for the reference electrode [43].

2.2.2. Experimental conditions

The experimental treatment conditions are detailed in Table 1. This study evaluates three distinct operation regimes: i) Recirculation, with leachate recirculation under anaerobic conditions; ii) Aeration, with aeration and no leachate recirculation. For Bra and Kra, aeration was followed by an anaerobic period; iii) Recirculation-Aeration, with a period of leachate recirculation under anaerobic conditions followed by a period of aeration without leachate recirculation. Prior to the start of above treatments, all LSRs had a 139-day anaerobic initialization period without gas input.

Anaerobic conditions were maintained by continuous N₂ gas

injection (2 ml/min). Leachate recirculation was applied at a rate of 1 L/week (approx. 20 times the field intensity at Kra); this applied rate was a combination of desired intensification of degradation and practical design limitations with respect to the equal distribution and pumping rate of the recirculated leachate. Aeration was achieved using compressed ambient air with a continuous flow of 10 ml/min (five times the target field rate for Bra and Wie).

For the Recirculation-Aeration LSRs, the operational mode switched to aeration after 139 days of initialization and 252 days of recirculation. To ensure effective aeration, accumulated leachate was gravimetrically drained prior to the switch. The aeration LSRs of Bra and Kra were reverted to anaerobic conditions (2 ml N₂/min) after 139 days of initialization and 435 days of aeration. Thus, potential leachate quality changes following the termination of aeration and the return of anaerobic conditions could be investigated.

To simulate rainfall, 500 ml of demineralized water was added every 2–3 weeks to all non-leachate recirculation LSRs; for anaerobic LSRs this water was purged with N₂ prior to addition to prevent oxygen ingress. The total water addition and rationale can be found in Section SM1 in

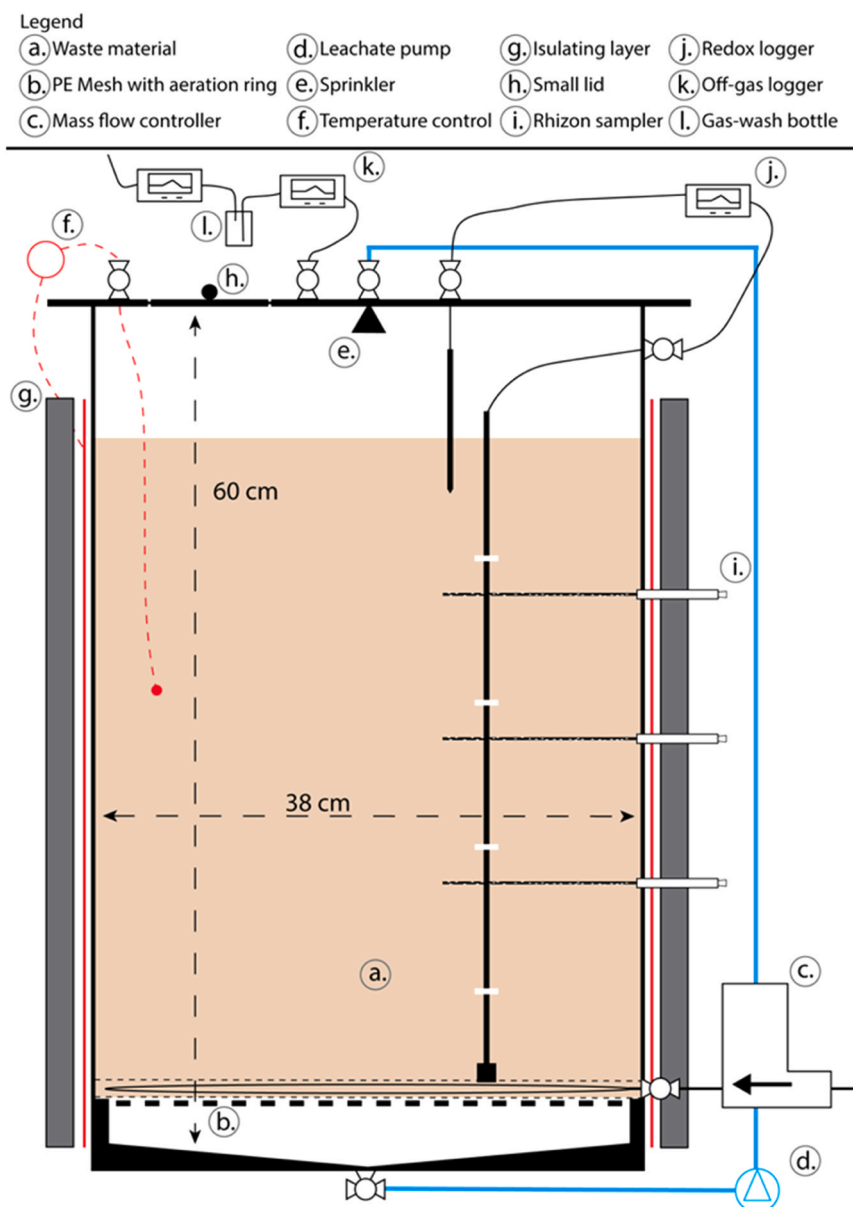


Fig. 1. Schematic overview of the landfill simulation reactors used in this study.

Table 1

Operational conditions of the landfill simulation reactors (LSR). Anaerobic conditions are annotated as An. Aeration is annotated as Ae. All treatments were preceded by a 139-day anaerobic initialization period without gas input.

Operational name	Condition (An/Ae)	Anaerobic period [days]	Aerobic period [days]	Gas input [ml/min]	Recirculation [l/w]
Recirculation	An	543	-	2 (N ₂)	1
Aeration ^a	Ae – An	108	435	2 (N ₂) + 10 (Air)	-
Recirculation-Aeration	An – Ae	252	291	2 (N ₂) + 10 (Air)	1 ^b

^a The aeration LSR of Wie was not returned to anaerobic conditions and was kept under aeration.

^b Recirculation was applied only under anaerobic conditions. When switched to aeration, recirculation stopped.

the SI.

2.2.3. Leachate sampling

A 5 cm reservoir between the perforated disc and LSR base (Fig. 1) allowed for leachate accumulation between sampling events. At each sampling round, 100 ml of leachate was collected. To ensure that samples represented the specific time interval between sampling rounds, all remaining leachate was gravimetrically drained from the non-recirculation LSRs following sample collection (implemented from the second sampling round onwards). Samples were stored at 4°C prior to analyses.

2.2.4. Solid phase sampling

To monitor solid phase changes, six sacrificial PP mesh bags (~250 g wet waste, 3 mm PP mesh) were embedded in each LSR. At three intervals during operation, a mesh bag was retrieved through the small lid on top of the LSRs, sieved (4 mm), and stored at 4°C prior to pretreatment and analyses.

2.3. Sample analyses

2.3.1. Leachate analyses

The pH and electrical conductivity were measured immediately upon collection. Samples were subsequently filtered through 0.45 µm cellulose filters and split into three aliquots. Chloride and NH₄⁺ were analysed on a discrete analyser (Skalar Bluvision, Analytical B.V., Breda, The Netherlands). From round 7 onwards, NH₄⁺, NO₂⁻ + NO₃⁻, and total N were measured using a segmented flow analyser (SFA, San++, Skalar Analytical B.V., Breda, The Netherlands). Other inorganic contaminants were, after acidification to a concentration of 0.14 M HNO₃, analysed on an Inductively Coupled Plasma – Optical Atomic Emission Spectrometer (ICP-OES iCAP 6500 DUO, Thermo Fisher Scientific Inc., Waltham, MA, USA) (Al, Ca, Cu, Fe, K, Mg, Mn, Na, P, Si, Zn) and High Resolution – Inductively Coupled Plasma – Mass Spectrometry (HR-ICP-MS Element 2, Thermo Fisher Scientific Inc., Waltham, MA, USA) (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Sb, Sr, V, Zn). The remaining aliquot was used to determine organic C (OC) by measurement of total and inorganic C (TC and IC respectively, where OC = TC - IC) using a SFA. In addition, this aliquot was subjected to rapid batch fractionation [44] to determine dissolved humic substances (HS: humic acid (HA), fulvic acid (FA), hydrophilic acid (Hy), and hydrophobic neutrals (HON)).

2.3.2. Chemical extractions of solid waste

Reactive solid phases were characterized using selective extractions on the mesh bag samples. Amorphous Al- and Fe (hydr)oxide contents were estimated via ammonium oxalate [45] and ascorbic acid [46] extractions, respectively; crystalline Al- and Fe (hydr)oxides were estimated using the dithionite extraction [47]. Concentrations of Al and Fe in the extracts were measured with an ICP-OES. The total amount of HS and its subfractions (HA, FA, Hy, HON) was determined through acid-base extraction followed by rapid batch fractionation [44] and subsequent OC determination with a SFA. Clay content was measured via the sieve and pipette method [48], yet not for the mesh bag samples. Finally, total reactive contaminant contents were determined by 0.43 M

HNO₃ extraction [49] and water-extractable concentrations by ultra-pure water (UPW) extraction (L/S 10) followed by analysis via ICP-OES and HR-ICP-MS for macro- and trace elements (see Section 2.3.1 for specific elements).

2.4. Geochemical modelling

Geochemical modelling was conducted in the modelling framework ORCHESTRA [50] in a similar set-up as van Raffe et al. [39]. This approach included modelling adsorption to reactive surfaces (HA, FA, Al- and Fe (hydr)oxides, clay) together with the formation of inorganic complexes and precipitation/dissolution of mineral phases based on the thermodynamic constants in the MINTEQA4 database [51]. Adsorption to HA and FA was modelled using the NICA-Donnan model [52], considering the generic parameters of Milne et al. [53,54] and taking the measured dissolved (Section 2.3.1) and solid (Section 2.3.2) HA and FA as input with an assumed carbon content of 50% [55]. Adsorption to Al- and Fe (hydr)oxides was modelled using the generalized two-layer model and generic parameters of Dzombak and Morel [56] taking hydrous ferric oxide (HFO) as a singular proxy for metal (hydr)oxides due to the limited database of Al (hydr)oxides [57]. The content of HFO was based on the measured quantities of amorphous and crystalline Al- and Fe (hydr)oxides (Section 2.3.2). For amorphous (hydr)oxides a molar ratio of 84 g Al/mol HFO, 95 g Fe/mol HFO [58], and a reactive surface area of 600 m²/g [56] was assumed. For the crystalline (hydr)oxides a molar ratio of 78 g Al/mol HFO, 89 g Fe/mol HFO, and a reactive surface area of 100 m²/g [56,59] was assumed. In line with van Raffe et al. [39], calculated HFO was corrected for binding to solid OM and dissolved OM based on separate model calculations and for dissolution of amorphous (hydr)oxides based on measured dissolved Al and Fe concentrations in solution. A further correction was made to account for sulphides in the anaerobic LSRs, as part of the initially determined oxides likely dissolved and formed sulphides and as during pretreatment of the waste in the mesh bags these sulphides may have partly dissolved and reformed as oxides; both instances result in an overestimation of the oxide content. To this end, HFO contents were halved based on the model-predicted relevance of Fe-sulphide formation (pH + pe < 8). Contrary to van Raffe et al. [39], adsorption to clay was modelled using a Donnan model, taking measured clay content as input and assuming all clay to be illite with a Donnan volume of 1 L/kg [60]. Additional inputs consisted of a calculated liquid:solid ratio (L/S), measured leachate pH, pe, dissolved concentrations of IC and competing elements, and reactive element concentration (0.43 M HNO₃ extraction) of the element of which the dissolved concentration is to be predicted, based on the aforementioned input parameters and in a similar fashion to van Raffe et al. [39]. The model was used to calculate the solid-solution partitioning and speciation of all analysed elements in both the solid and solution phase for three distinct datasets: LSR leachate (Section 2.3.1), the pH-dependent test (Section SM2, SI), and the mesh bag extracts (Section 2.3.2). Findings from the latter two experiments were used to build the modelling framework of the LSR leachate modelling (Section SM3, SI); the LSR leachate modelling is described below.

The LSR leachate was modelled as a well-mixed batch system. While the LSRs are dynamic systems, we believe this batch equilibrium

approach was appropriate as the leachate was collected on average over a period of one month between sampling rounds, following which leachate was fully drained from the LSRs. Each leachate sample was thus a representation of the entire LSR for the entire period between sampling rounds. The L/S ratio was calculated based on a mass balance approach, with total liquid calculated from added (initial water and added e.g. through rain simulation) and removed water (drainage and leachate sampling), and the solid weight being the initial dry weight minus the dry mass removed with the mesh bags. Dissolved element and OM concentrations together with pH were measured in the leachate samples. The redox potential (pe) measured at 7.5 cm from the bottom of the waste was used as model input, as the measured redox potential was relatively consistent throughout the LSRs and the conditions at the bottom most strongly dictate the leachate quality. The solid reactive surfaces and reactive elements content was set to those determined in the mesh bag extractions; for leachate sampling rounds where mesh bags were not sampled, inputs were set equal to the last round in which mesh bags were analysed. Assumed mineral forms in the modelling were based on van Raffe et al. [39] and listed in Table S2.

3. Experimental and modelling results & discussion

3.1. General parameters

Operational conditions (Table 1) significantly influenced the redox potential (Fig. 2). Under leachate recirculation, strongly reducing conditions ($pe \approx -7.5$) prevailed irrespective of waste origin. In contrast, continuous aeration led to a steady increase in redox potential, stabilizing at different plateaus for the different wastes: $pe \approx 0$ for Kra, $pe \approx 3$ for Bra, and a two-step increase for Wie ($pe \approx -1$ then ≈ 3). The Recirculation-Aeration treatment resulted in a more rapid oxidation for Kra and Wie compared with continuous aeration. Here Kra exhibited a two-step increase ($pe \approx 0$ then ≈ 5), while Wie directly increased to stabilize at the same level as for continuous aeration ($pe \approx 3$). This accelerated response is likely due to the drainage step performed before switching the operational conditions, which effectively removed dissolved reductants. Unexpectedly, the Bra Recirculation-Aeration LSR showed no distinct increase of the redox potential after the switch to aeration. This absence is probably due to compaction of the finer, clay-rich waste during leachate recirculation restricting gas permeability, as this compaction was observed during waste sampling upon LSR

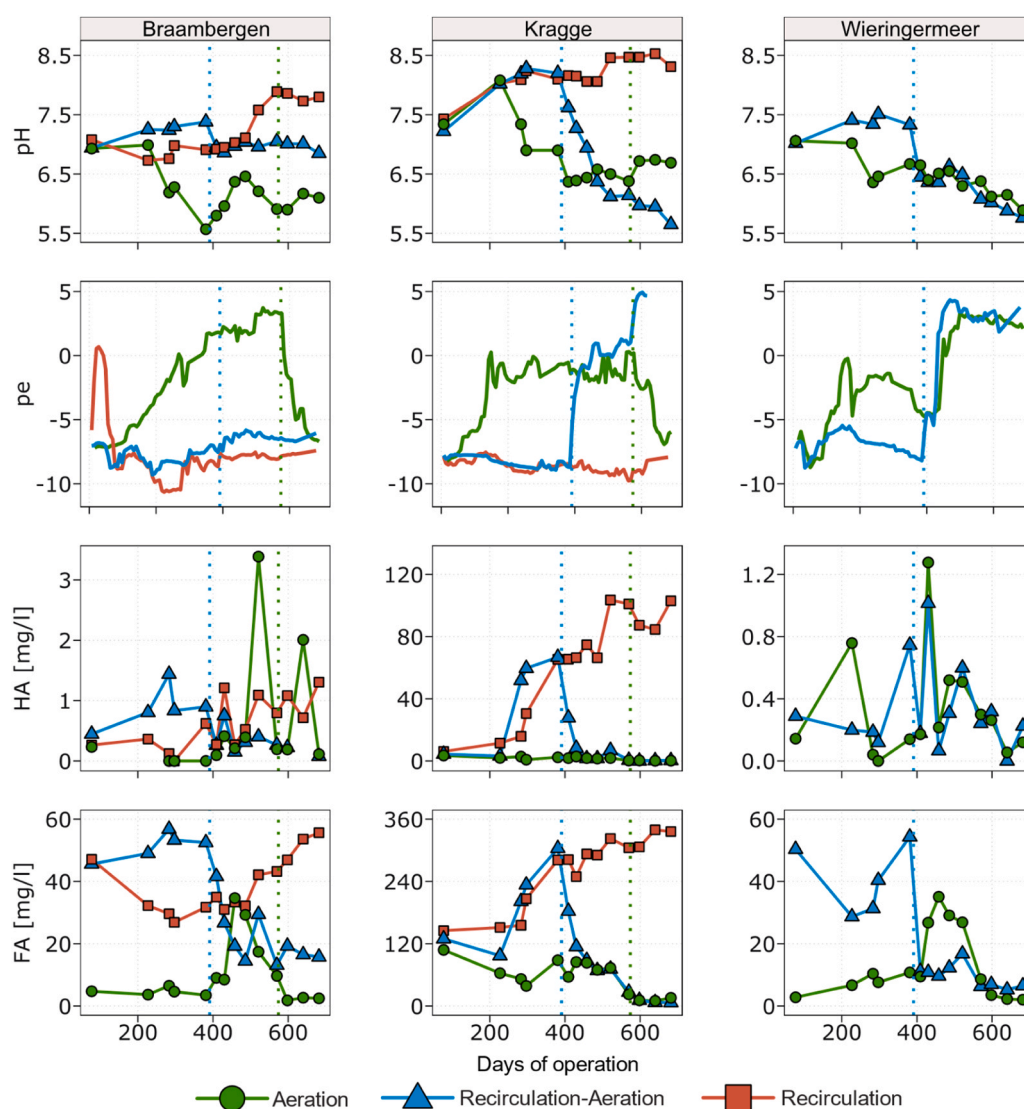


Fig. 2. Measured changes in general parameters in the landfill simulation reactors during the operation under different operational conditions. The vertical dotted lines indicate the date at which the Recirculation-Aeration LSR switched from recirculation to aeration (blue) and when the aeration LSRs of Braambergen and Kragge switched from aeration to anaerobic conditions (green).

termination.

Leachate pH increased slightly during recirculation, exceeding 8.0 (Fig. 2), a value characteristic of methanogenic or stable phase landfills [61]. Conversely, aeration caused a pH decrease, consistent with previous LSR studies [35,62]. This acidification is likely driven by the production of organic acids during stimulated OM degradation [63] and proton release during nitrification [64,65].

Reactive organic matter fractions (HA and FA) increased in concentration during recirculation (Fig. 2), correlated with the observed increased pH [39]. The lower HA and FA concentrations under aeration are attributed to stimulated microbial degradation and the observed decreasing pH (Fig. 2).

3.2. Inorganic contaminants

Inorganic contaminant concentrations in the LSR leachate showed a strong dependence on operational conditions (Fig. 3 & Figure S7), driven by the previously described shifts in redox potential, pH, and dissolved HS. Based on mechanisms identified in the pH-dependent leaching tests (Section SR1) and mesh bag extracts (Figures S4 & S5), contaminants were categorized as anionic and two cationic subdivisions based on i) redox sensitivity and ii) the observed pH of minimum solubility (Figure S2). The geochemical model generally captured the observed leaching trends (Figure S9), yet root mean square error (RMSE) [66] values frequently exceeded 1 (Figure S10), indicating strong deviations between model calculations and measurements which are discussed below.

3.2.1. Reactive anions

Anionic contaminant concentrations, represented by As (Fig. 3), generally remained stable under recirculation and decreased under aeration. The geochemical model adequately predicts these trends, identifying adsorption to Fe/Al (hydr)oxides as the controlling mechanism for all operational conditions (Fig. 4). The observed decrease in As leachate concentrations during aeration is attributed to increased anion adsorption to these Fe/Al (hydr)oxides at the lower pH [67,68]. This pH-dependency was clearly demonstrated in the pH-dependent test (Figure S2) and best exemplified by the Bra aeration LSR, where a minor pH increase around day 500 (Fig. 2) triggered a simultaneous spike in anionic concentrations (Fig. 3 and Figure S7). In addition to changing pH, the oxidation of Fe-sulphides during aeration may have induced the (neo)formation of metal (hydr)oxides [69] and thereby provide additional binding sites, which further explains the observed reduced anion mobility during aeration.

The other anionic contaminants (Mo, Sb, and P) all showed a similar decrease in concentrations during aeration, albeit with an initial increase in Mo and Sb concentrations (Figure S7). This was again predicted to be predominantly controlled by Fe/Al (hydr)oxide binding and a predicted formation of calcium-phosphate minerals for P (Figure S12). Under leachate recirculation Mo and Sb concentrations decrease and P concentrations increase, with the contrary result of the latter potentially related to organic P mineralization, as was previously found under anaerobic conditions [70], or due to a stronger pH dependence of P at a pH of 8 (Figure S2).

3.2.2. Reactive cations

Cationic contaminants can be distinguished based on their response to a changing redox potential (via changes in their valency or changes in the stability of sulphide minerals) and their pH of minimum solubility (Section SR1, SI).

3.2.2.1. Redox sensitive cationic contaminants. Concentrations of redox sensitive cations, represented by Fe, were stable under leachate recirculation and initially increased and subsequently decreased under aeration (Fig. 3). The geochemical model predicted Fe to be present as a

sulphide mineral under the anaerobic conditions of leachate recirculation (Fig. 4). Upon aeration, the model predicted an increase in Fe concentrations due to sulphide oxidation and mineral dissolution, followed by a decrease in Fe concentrations due to the predicted precipitation of first carbonate and then (hydr)oxide minerals (Figure S13). This order of mineral precipitation is consistent with predicted Fe behaviour in anaerobically deposited soils [71].

The reversibility of the above mechanisms can be observed for the Bra and Kra Aeration LSRs, which return to anaerobic conditions on day 591 caused a spike in leachate Fe concentrations (Fig. 3) as formed Fe-(hydr)oxides likely re-dissolved as Fe^{2+} . The model captured this dissolution, yet predicted a rapid re-formation of Fe-sulphides and a corresponding drop in Fe concentrations (Fig. 4 & Figure S13). This drop is not yet observed in the measurements, suggesting a kinetic lag.

Other redox sensitive metals (Cd, Cu, Mn, and Zn) similarly increased and then decreased during aeration. The initial increase is for all predicted to be a result of sulphide mineral dissolution, while the subsequent decrease is either a result of mineral formation (Mn) or binding to reactive surfaces (Cd, Cu, Zn) (Figure S12). Notably, the mesh bag extracts only showed a clear redox sensitivity for Fe and Cu (Figure S5), which could only be modelled accurately by adjusting $\text{pe} + \text{pH}$ values upwards to account for oxidation during sampling and storage (Section SM3).

3.2.2.2. Reactive cations with a solubility minimum below pH 8. Cationic elements with a solubility minimum below pH 8, exemplified by Cr (Fig. 3), generally increased in concentration in the recirculation LSRs and decreased in concentration in the aeration LSRs. These trends parallel trends in HS solubility (Fig. 2), consistent with model predictions that identify binding to dissolved HS (Fig. 4) as the primary control mechanism for Cr [72,73]. Similar behaviour was observed for Sn and Al in Kra LSRs, which are similarly characterized by a high affinity for OM binding [54,74].

3.2.2.3. Reactive cations with a solubility minimum between pH 8 and 10. For cationic elements with a solubility minimum between pH 8 and 10, represented by Ni (Fig. 3), concentrations generally increased (Kra) or remained stable (Bra & Wie) in the recirculation LSRs. During aeration, concentrations initially increased and later decreased. The model poorly predicted these dynamics, predicting Ni to be predominantly bound to Fe/Al (hydr)oxides and OM (Fig. 4 & Figure S11) yet with a high uncertainty considering the poor predictions. The observed differing behaviour of Ni during leachate recirculation for the different waste is in likelihood related to the different pH of minimum solubility. For Kra this pH of minimum solubility is decidedly lower than for Bra and Wie (Figure S2), related to its higher OM content [39]; the increasing pH under recirculation thus moves away from minimum solubility and results in increasing concentrations. For Bra and Wie the pH hovers around the minimum, resulting in stable concentrations.

The initial Ni concentration increase observed during aeration likely resulted from an increased competition for surface binding sites following mineral dissolution of other elements, specifically the release of Fe upon sulphide dissolution and the subsequently discussed Ca release upon carbonate dissolution. This influx of competing ions can displace Ni, temporarily increasing the leachate concentration. The subsequent decline in Ni aligns with the eventual decrease of these competing elements, alongside a decrease in pH and dissolved HS concentrations (Fig. 2). The inability of the model to capture this 'peak' trend suggest that the assumed system equilibrium may not be valid during rapid geochemical shifts. Si and Co showed similar trends (Figure S7), although Si is predicted to be controlled by the formation of silicate minerals rather than surface complexation (Figure S12).

3.2.2.4. Reactive cations with a solubility minimum above pH 10. Cationic elements with a solubility minimum above pH 10, exemplified by Mg

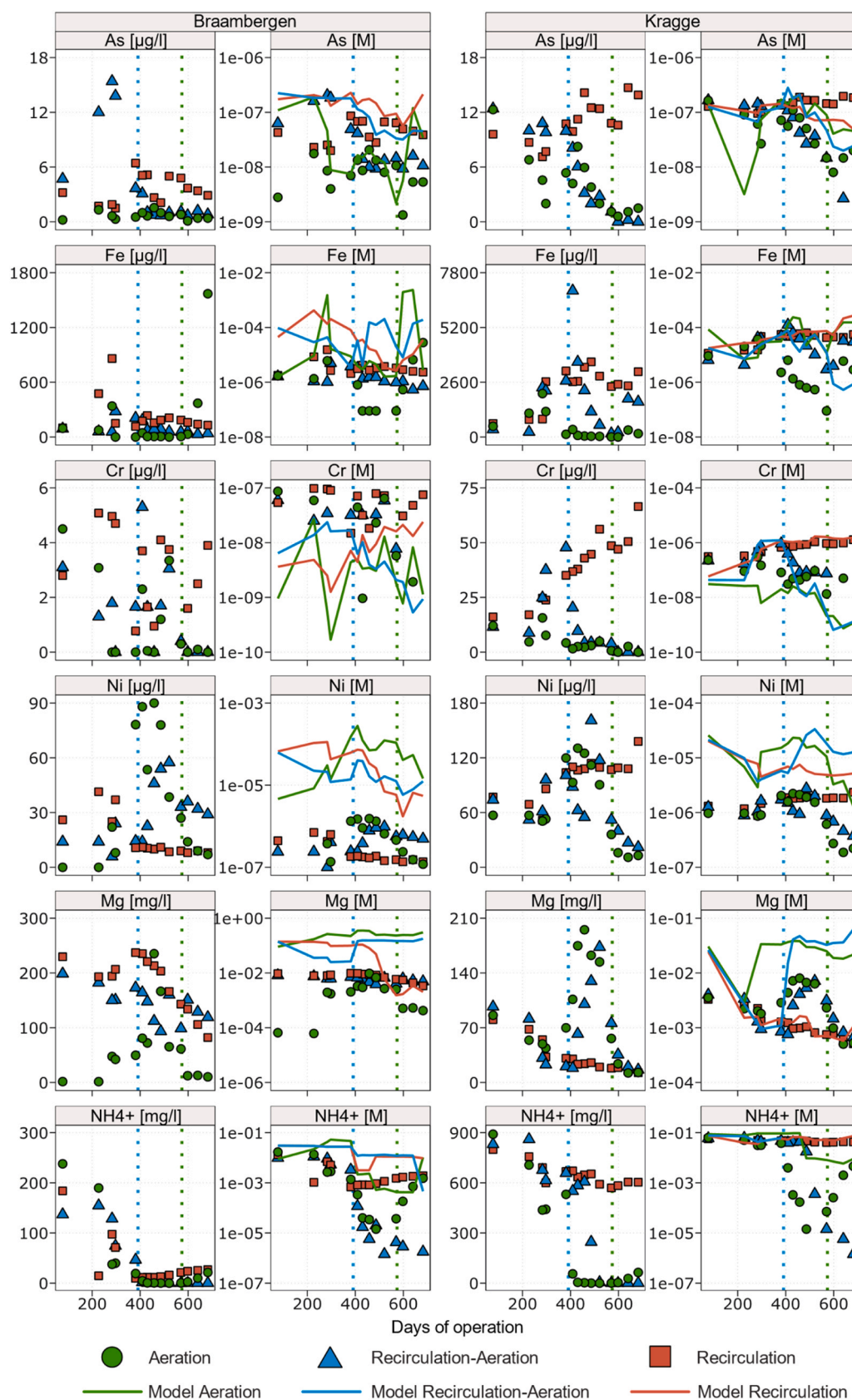


Fig. 3. Measured (symbols) and modelled (lines) concentrations of contaminants in the LSR leachates during LSR operation under different operational conditions. The vertical dotted lines indicate the date at which the Recirculation-Aeration LSR switched from recirculation to aeration (blue) and when the aeration LSRs of Braambergen and Kragge switched from aeration to anaerobic conditions (green).

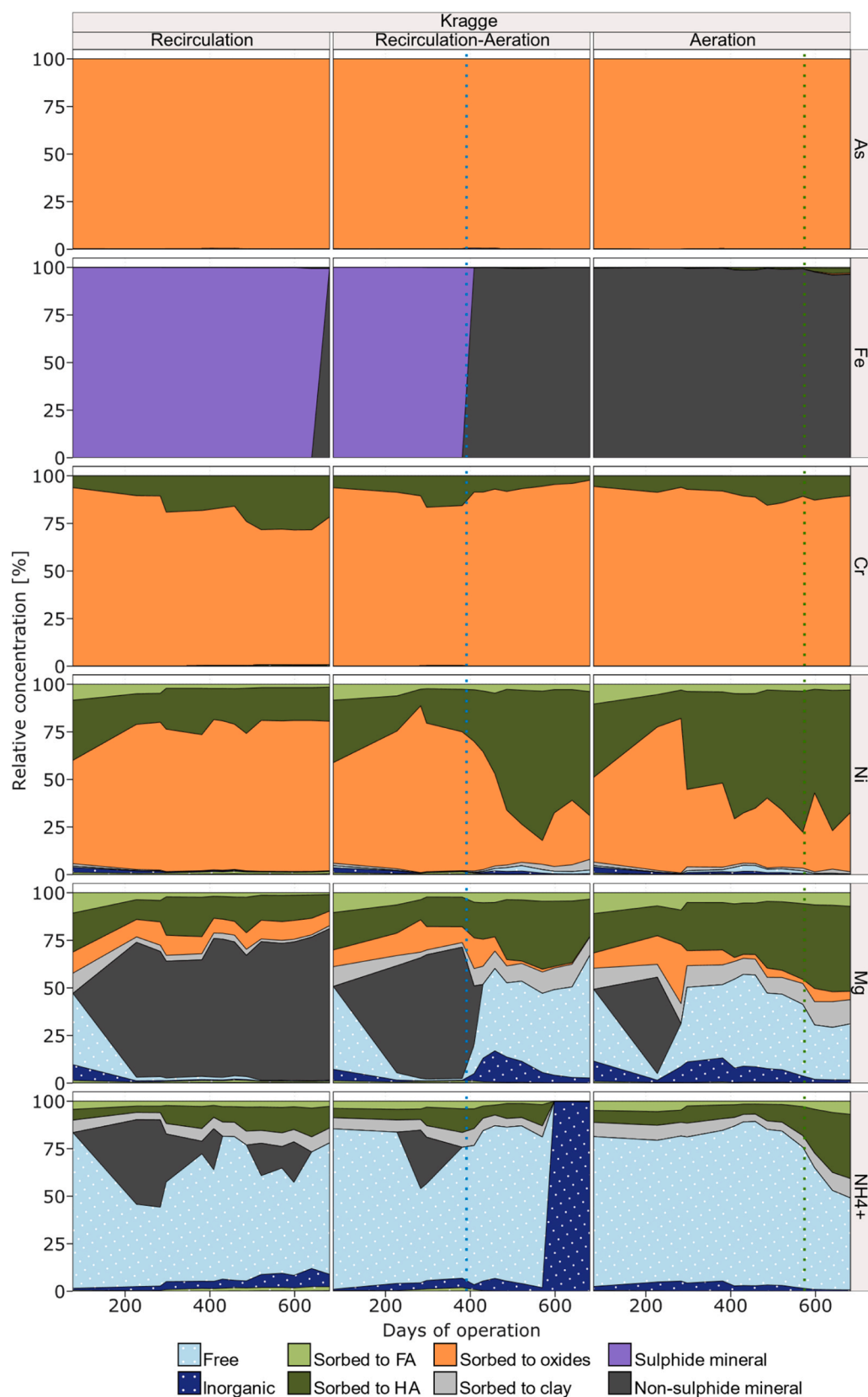


Fig. 4. Model calculated solid and dissolved phase speciation of contaminants in the Kragge LSRs as a function of time. The vertical dotted lines indicate the date at which the Recirculation-Aeration LSR switched from recirculation to aeration (blue) and when the aeration LSRs of Braambergen and Kragge switched from aeration to anaerobic conditions (green). White dots represent dissolved species.

(Fig. 3), decreased in concentration in the recirculation LSRs and increased before subsequently decreasing in the aerated LSRs. The geochemical model predicts these trends to be predominately steered by mineral precipitation as either struvite or sepiolite (Fig. 4). Under leachate recirculation, the elevated pH (Fig. 2) promotes mineral precipitation [39], thereby reducing leachate concentrations. Conversely, the release of Mg during aeration likely stems from mineral dissolution at lower pH and reduced availability of co-precipitating elements. The subsequent decrease under aerated conditions was not captured by the model. Potentially this is the result of a disconnect between the waste mass (where mineral precipitation occurs) and the leachate (on which calculations are based). Other contaminants in this group include Ba, Sr, and Ca, all of which followed similar patterns (Figure S7), yet with differing controlling minerals (sulphates for Ba, carbonates for Sr and Ca) (Figure S12).

3.2.3. Ammonium

Ammonium (NH_4^+) tends to accumulate in landfill leachate due to the absence of nitrification as a removal pathway under anaerobic conditions [75,76], making it the contaminant of primary concern [9,14]. In the LSRs NH_4^+ concentrations decreased under both leachate recirculation and aeration, with a more pronounced decline during aeration (Fig. 3) related to differences in underlying mechanisms. During leachate recirculation the observed decrease is likely driven by struvite precipitation, as pH increased towards the struvite solubility minimum (around pH 8.5 [77]) and P concentrations were elevated under leachate recirculation (Figure S7). The geochemical model only predicted struvite formation for Kra (Fig. 4 and Figure S17), however here model predictions of NH_4^+ were also most accurate (Fig. 3). Under aerated conditions the observed decrease of NH_4^+ is attributed to nitrification, where NH_4^+ is oxidized to nitrate (NO_3^-) by nitrifying bacteria, a pathway well-documented in aerobically treated waste [78–80]. This is corroborated by the corresponding increase in NO_3^- concentrations in the leachate (Figure S18). Curiously, this increase is less pronounced when aeration was preceded by leachate recirculation; the waste in the Recirculation-Aeration treatment was likely sufficiently moist shortly after the switch in conditions and thus promoted simultaneous nitrification-denitrification.

3.2.3.1. The role of competing reductants and growth lag period. A multitude of studies – varying in LSR size, waste composition, and aeration intensity – have similarly demonstrated the potential of aeration to reduce NH_4^+ concentrations [16,18,21,28,65,81–86]. Remarkably, the required aeration period before NH_4^+ concentrations decreased was relatively consistent across studies at approximately 100 days. Considering the vast range of aeration intensities applied (from 22 ml/kg/h in this study to 4800 ml/kg/h [65]), this consistency suggests that the oxidation of competing reductants (e.g. OM and sulphides [87]) and the growth of nitrifying bacteria [88] are rate-limiting steps for nitrification, rather than oxygen availability. This hypothesis explains why Cossu et al. [89] did not observe a decrease in NH_4^+ despite applying an aeration rate of 208 ml/kg/h for 90 days; the duration was likely insufficient to exhaust the competing reduced species and facilitate the growth of nitrifying bacteria. This is further supported by studies where aeration was not preceded by an anaerobic initialisation phase or where, instead of sampled landfill waste, synthetic waste was used. In such cases reduced species did not accumulate, and the aerobic microbial community did not switch their metabolism to a very low rate to survive anaerobic conditions [90]. Correspondingly, aeration allowed for an immediate oxidation of and steep decline in NH_4^+ [82–84]. Nitrification inhibition by sulphides may have further obstructed the removal of NH_4^+ [91,92]. This effect is well illustrated by the Recirculation-Aeration LSRs in this study: the drainage of leachate removed a significant load of dissolved reductants, facilitating more effective aeration and oxidation of sulphides which resulted in a more

rapid decline of the NH_4^+ concentrations (Fig. 3).

3.2.3.2. Rebound effects. The efficiency of aeration for NH_4^+ removal is widely recognized [93,94], yet to adhere to legislation criteria the permanence of this removal is critical. A return of the Aeration LSRs of Bra and Kra to anaerobic conditions resulted in a rebound of NH_4^+ concentrations due to ongoing (anaerobic) OM degradation (Fig. 3). This rebound effect has been noted previously [18], but was deemed limited and related to a significantly increased NH_4^+ sorption capacity of aerated waste. We found no indication of an increased sorption capacity but rather determined a reduced reactive surface area for our aerated waste (Quist et al., in prep). As such, achieving a permanent reduction of NH_4^+ concentrations via aeration requires the complete removal of the degradable waste fraction, rather than temporary aeration.

4. Discussion on field scale implications

4.1. Identifying mechanisms underlying contaminant solubility

The previously identified mechanisms aligned closely with those observed in the pore water of the leachate recirculation pilot landfill *De Kragge* [40]. This consistency highlights the value of controlled *ex situ* LSR set-ups in interpreting complex *in situ* processes, as the LSRs allow for a detailed analysis of the solid-phase and the use of measured, rather than assumed, redox potentials. This approach revealed the redox sensitivity of Mn and Cd, which was not identified by van Raffe et al. [40]. This discrepancy suggests that the true impact of redox conditions may be obscured during sample transport and handling, as also evidenced by the limited redox sensitivity observed in the mesh bag extracts and the pH-dependent test (Section SR1, SI).

It should be noted that the studied waste composition represents countries with highly developed waste collection systems. Nevertheless, the underlying geochemical mechanisms observed here may be largely universal. The insights obtained should therefore be translatable to waste of different origins, even if the dominance of specific solubility-steering mechanisms varies.

4.2. Achieving effective reductions in contaminant concentrations

The operational conditions employed in this study highlight the importance of hydrology in active landfill treatment. In the Recirculation-Aeration LSRs, the intermediate drainage of leachate rich in reduced species resulted in rapid changes in redox conditions, thereby accelerating the onset of nitrification and corresponding NH_4^+ removal. This suggests that the implementation of aeration as an active treatment strategy could be significantly optimized by actively controlling the hydrological conditions within landfill bodies. The accelerated response must, however, be framed carefully; the observed faster transition following leachate drainage does not necessarily equate to greater overall treatment effectiveness.

An important note on active treatment effectiveness was demonstrated by this study in the distinct trade-off for both the Aeration and the Recirculation-Aeration treatments. The (rapid) reduction in NH_4^+ was counterbalanced by the transient mobilization of other contaminants. Parallel sulphide oxidation resulted in temporary concentration peaks for several redox-sensitive elements, including Cd, Cu, Fe, Mn, and Zn. With progressive aeration, the concentrations of these elements returned to pre-aeration levels as they either adsorbed to solid reactive surfaces or precipitated as (oxide) minerals. Ultimately, while Recirculation-Aeration improved the kinetic response to aeration, it still induced the transient mobilization of contaminants. Furthermore, the long-term durability of these outcomes after active treatment ceases (e.g. the risks of an NH_4^+ rebound effect) remains a critical consideration for overall environmental protection.

4.3. Limitations

4.3.1. Translation of landfill simulation reactors to the landfill scale

While the LSRs provided valuable insights into mechanisms controlling contaminant solubility, direct translation to the field is complicated by their small scale, which cannot capture the complex hydrology and heterogeneity of full-scale landfills [28,95]. A significant difference is the presence of preferential flow paths; for example, approximately 20% of water infiltrating *De Kragge* landfill leaves the waste body as leachate within 45 days [96]. Preferential flow means only specific waste regions are reached, and the limited contact time prevents equilibrium between waste and water, thereby heavily impacting contaminant dynamics. The filling materials in the LSRs were specifically engineered to limit this preferential flow, ensuring highly controlled experimental conditions but inherently dampening and transforming the physical and hydrological heterogeneity present at field scale.

A clear effect of the LSR scale was evident in the ‘uniform’ redox conditions. The LSRs were either fully aerobic or anaerobic due to the continuous introduction of compressed air or N_2 gas, and switching between gases resulted in a rapid transition of redox states. In contrast, full-scale landfills simultaneously contain aerobic and anaerobic pockets [97] and are thereby subject to a complex interplay of reducing and oxidizing mechanisms. Because of this interplay, the distinct contaminant concentration peaks in the LSRs will likely not occur to the same extent in the field. Instead, a dampened, continuous increase in concentrations is expected, followed by a gradual decrease. This will potentially result in an extended timeframe of elevated concentrations, though the peak levels will likely remain lower than those observed in the LSRs.

Effective translation to the field scale will require assessing landfill heterogeneity and hydrology, as well as linking the solubility-controlling processes identified in this LSR study to chemical compositional changes in landfill leachates, specifically where field-scale applications of aeration (*Braambergen & Wieringermeer*) and leachate recirculation (*Kragge*) are being tested.

4.3.2. Equilibrium modelling

The mechanisms behind contaminant leaching were interpreted via geochemical modelling. Because geochemical model calculations rely on the concept of chemical equilibrium [98–100], meaningful calculations for natural systems require the modelled system to be at least in a state of local (and/or pseudo-) equilibrium, even though the system as a whole may not be in true thermodynamic equilibrium. While conditions within the LSRs were largely stable, aeration, particularly when preceded by leachate recirculation, induced a sharp transitional phase until a new steady state was reached. Such active transitions, in particular, cannot be definitively modelled based on a chemical equilibrium assumption.

4.4. Implications for active treatment termination

The ultimate goal of active treatment is to reduce contaminant concentrations below established ETVs, ensuring that residual emissions do not pose environmental harm [13,14]. The current ETV determination assumes a ‘worst-case’ scenario where emissions remain constant upon the termination of active treatment. However, our results challenge the applicability of this assumption.

In the aeration LSRs of Bra and Kra, conditions were reverted to an anaerobic state after 574 days. Within days, concentrations of NH_4^+ and Fe rebounded. This return to anaerobic conditions is a likely scenario in full-scale landfill bodies once active aeration ceases and residual oxygen is consumed. Consequently, reliance on leachate concentrations alone is insufficient for determining a safe termination point for active treatment. A full understanding of the remaining emission potential of the landfilled waste should be derived not only from developments in leachate concentrations, but also from the evaluation of the evolving

characteristics of the solid phase that ultimately control contaminant mobility.

5. Conclusion

This study elucidated the geochemical mechanisms governing hazardous contaminant leaching from landfill waste, demonstrating how these mechanisms drive changes in contaminant mobility during active treatment via aeration and leachate recirculation. By coupling landfill simulation reactors and pH-dependent leaching tests with state-of-the-art multi-surface geochemical modelling, we quantified the critical roles of pH, redox potential, mineral formation/dissolution and organic matter leaching in controlling contaminant solubility.

The impact of the specific treatment conditions was distinct. Leachate recirculation maintained strongly reducing conditions and stable humic substance concentrations, and generally increased pH. Consequently, the concentration of multiple contaminants increased due to pH-driven solubility shifts, while sulphide mineral precipitation controlled the solubility of redox-sensitive elements. Conversely, aeration lowered the pH and decreased concentrations of both organic and inorganic C as the system became increasingly aerobic. This resulted in an initial increase in contaminant concentrations due to mineral dissolution, followed by a decrease driven by binding to reactive surfaces and the formation of new mineral precipitates (e.g. metal (hydr)oxides).

Crucially, the system response to aeration was markedly quicker when preceded by leachate recirculation and subsequent leachate drainage. This Recirculation-Aeration strategy effectively removed dissolved reductants prior to aeration, highlighting the importance of adequate landfill drainage in accelerating field response to active treatment.

Aeration proved most effective for decreasing NH_4^+ and dissolved OM yet introduced a critical trade-off: the temporary mobilization of redox-sensitive contaminants, which at peak levels exceeded emission target values. Furthermore, returning the aerated LSRs to anaerobic conditions resulted in a rebound in NH_4^+ & Fe concentrations, challenging the assumption that active aeration guarantees permanent stabilization. Therefore, the environmentally safe termination of active treatment cannot rely solely on leachate monitoring. It requires a robust characterization of the solid waste’s emission potential to ensure that the return to anaerobic conditions does not result in a future exceedance of emission target values.

Environmental implication

Current management of waste landfills requires encapsulating the waste with impermeable layers, protecting the environment yet requiring continuous monitoring and layer replacement. Actively reducing contaminant emissions via aeration and/or leachate recirculation is a more sustainable alternative, and its potential is shown in our study. Particularly aeration resulted in a strong decrease in the leachability of specific contaminants, yet this decrease was paired with an increase in other contaminants. Furthermore, a return to anaerobic conditions of aerated waste resulted in a re-increase of concentrations. Environmentally safe and sustainable management of waste thus requires a robust characterization of the waste’s emission potential.

CRedit authorship contribution statement

Joris J. Dijkstra: Writing – review & editing, Supervision, Formal analysis. **Rob N.J. Comans:** Writing – review & editing, Supervision, Funding acquisition, Formal analysis. **Frank van Raffe:** Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Formal analysis, Conceptualization. **Nick Quist:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Frank van Raffé reports financial support was provided by Dutch Research Council. Nick Quist reports financial support was provided by Dutch Research Council. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2026.142532](https://doi.org/10.1016/j.jhazmat.2026.142532).

Data availability

Data will be made available on request.

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