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# SARDINIA2023 19th INTERNATIONAL SYMPOSIUM ON WASTE MANAGEMENT AND SUSTAINABLE LANDFILLING 9-13 OCTOBER 2023 / FORTE VILLAGE RESORT

## UNDERSTANDING NITROGEN TRANSFORMATION USING THE RATIO OF NITROGEN TO ARGON IN LANDFILLS UNDER **IN-SITU STABILISATION**

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ABSTRACT: In the Netherlands, three full-scale pilots have been in operation for approximately five years to understand the effects of leachate recirculation or aeration on waste stabilisation. This study employs the ratio of N2 to Ar in the landfill gas in comparison to the ratio in atmospheric air to derive the share of N2 that originates from denitrification. We collected samples from the three pilot landfills from different gas wells, gas collector systems and from the total bulk extracted gas and measured its composition using gas chromatography. We estimated the aeration efficiency of the two landfills under in situ aeration based on the CO2/CH4 ratio as an indicator of aerobic processes. Denitrification dominated in the aerated landfills, with as much as 13% of N2 being explained by the net effect of denitrification, whereas the landfill under leachate recirculation showed a net 'loss' of N2 in the gas phase, indicating N2 fixation in the waste body to be a dominant mechanism. There was a seasonal variability of the balance between denitrification and N2 fixation in the aerated sites, likely caused by increased aeration efficiency and hence increased availability of NO3- for denitrification under summer conditions with lower moisture content in the cover soil, allowing for increased air ingress. No such variability was observed for the landfill under liquid recirculation. Future evaluation of the microbial community composition will further elucidate N transformation pathways in landfills under different in-situ stabilisation treatments.

Keywords: Denitrification, nitrogen fixation, aeration, leachate recirculation, tracer gas

#### 1. INTRODUCTION

One of the goals of a landfill in situ stabilisation programme (iDS, n.d.) on three full-scale landfills in the Netherlands is the long-term reduction of nitrogenous compounds and, thereby, of NH<sub>4</sub><sup>+</sup> (ammonium) concentrations in the leachate. This may be achieved by either enhanced leaching of NH4<sup>+</sup> through flushing with water and/or recirculated leachate (landfill de Kragge), or by transforming NH4<sup>+</sup> into nitrite (NO<sub>2</sub><sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), nitrous oxide (N<sub>2</sub>O) and to N<sub>2</sub> as the final product in the case of landfill aeration (landfills Braambergen and Wieringermeer). In both cases, the NH<sub>4</sub><sup>+</sup> can also be transformed to N<sub>2</sub> by anaerobic ammonium oxidation. Any nitrate can be emitted via the leachate or denitrified to N<sub>2</sub>O and N<sub>2</sub>, then leaving the waste body via the gas phase. Aerated landfills have been shown to be a significant contributor to N<sub>2</sub>O emissions (Chu et al., 2022) as it is a final product of nitrification and as an intermediate product of denitrification.

While the concentrations of nitrogen species in the leachate ( $NH_4^+$ ,  $NO_3^-$  and  $NO_2^-$ ) are straightforward to monitor, the share of nitrogen leaving the waste body via the gas phase as molecular nitrogen ( $N_2$ ) is less easy to quantify as  $N_2$  in the extracted or emitted gas originates, to a large extent, from atmospheric air, especially in the case of actively aerated landfills. Adequate mass balancing of nitrogen transformations requires that all potential N pathways within the in-situ stabilisation processes can be quantified. There is more research available that explains  $N_2O$  than  $N_2$  production from landfills (Chu et al., 2022; Harborth et al., 2013; Li et al., 2017b, 2017a; Sun et al., 2013; Zhang et al., 2009).  $N_2$  is not a greenhouse gas, however, to estimate the reduction of a landfill's emission potential by in situ stabilisation regarding nitrogen, it is of interest to quantify the share of nitrogen that is removed via the gas phase.

In this study, we used argon as a tracer to estimate the share of N<sub>2</sub> originating from the waste body. The only source of the noble gas argon (Ar) in extracted landfill gas is atmospheric air, while N<sub>2</sub> in the extracted landfill gas can originate from the atmosphere but also from denitrification within the waste body. Enrichment in N<sub>2</sub> in relation to Ar (compared to their ratio in atmospheric air) indicates N<sub>2</sub> released from denitrification while depletion of N<sub>2</sub> in relation to Ar (compared to their ratio in atmospheric air) indicates N<sub>2</sub> released from denitrification. For this reason, the ratio between Ar and N<sub>2</sub> can be used to estimate the (additional) share of N<sub>2</sub> originating from denitrification or the share of N<sub>2</sub> 'lost' by N<sub>2</sub> fixation (Nagamori et al., 2016; Shigemitsu et al., 2016). As part of the project CURE (NWO, 2019), this study presents the net balance between these processes from landfills de Kragge, Braambergen and Wieringermeer based on the analysis of gas samples from individual gas wells and the bulk extracted gas, collected in 2022 and 2023. The study hypothesised that denitrification or denitrification coupled to nitrification would deliver N<sub>2</sub>O and N<sub>2</sub> to the extracted landfill gas.

#### 2. LANDFILLS UNDER INVESTIGATION

Three Dutch landfills were investigated to determine the effects of in-situ stabilisation on speciation of nitrogenous gases: de Kragge (KRA, opereated by Attero B.V.), Braambergen (BRA) and Wieringermeer (WIE), the latter two operated by Afvalzorg Holding. All three sites have selected compartments dedicated to conduct full-scale in situ stabilisation pilot studies. The landfills will be referred to as KRA, BRA and WIE herein.

KRA landfill stores ~1 million tonnes of construction and demolition wastes, commercial and domestic wastes, but the pilot compartment is dominated by domestic waste. KRA landfill uses recirculation of the outflow from the nitritation unit of the wastewater treatment plant to expedite waste degradation. Leachate circulation at KRA started on March 2018.

BRA landfill stores ~1.2 million tonnes of waste consisting of construction and demolition wastes, contaminated soils, and soil residues (Cruz et al., 2021; Lammen et al., 2021). The landfill operates four pilot compartments 11 North (11N) and South (11Z), and 12 East (12O) and West (12W). BRA landfill applies a system that both injects and extracts air into the waste body to enhance waste degradation into four compartments. The oldest compartment is 12W. Compartments 12O and 11Z comprise mainly of soil and contaminated soil residues. Compartment 12W and 11N includes commercial waste and other household waste. At BRA, in-situ aeration is carried out using 230 wells spaced 15 to 20 m distance. The wells are bundled to a small number of pipes from which the bulk is extracted or through where the air is injected. In this study, all samples are clustered into to the three compartments they originate from (11N, 11Z and 12) and into bulk extracted gas (bulk mixture of all compartments).

WIE landfill contains ~350 thousand tonnes of commercial wastes, sludges and composting materials and contaminated soils, but the treated compartment consists mostly of industrial, building and demolition wastes. WIE pilot landfill operates by creating an under-pressure in the system through over-extraction of landfill gas, thus allowing ambient air to intrude into the wastes through the cover soil. The gas is extracted from two compartments (C6 and part of C5A) at -20 to -40 hPa from a total of 109 gas wells with a mean flow rate ranging between  $2 - 5 \text{ m}^3$ /h per well in an area of ~2.6 ha (Gebert et al., 2023).

Rainwater infiltrating into the three landfills is approximately 300 mm/year according to the average

Dutch net infiltration rates (Brand et al., 2014). The mean winter temperatures were  $\sim$ 3°C and the mean summer temperatures were  $\sim$ 17°C.

#### 3. METHODS

#### 3.1 Sample collection

All gas samples were collected between August 2022 to February 2023 from individual gas wells and from the bulk gas extraction piping. Using a gas-tight syringe, 10 ml of gas was injected through a rubber septum fixed with a screw cap into glass vials filled with acidified distilled water (pH 1.8). The vials were stored upside down until further analysis. The gas samples were analysed for gas components  $CH_4$ ,  $CO_2$ ,  $N_2O$ , Ar,  $O_2$ , and  $N_2$  using a gas chromatograph (Agilent 8860 GC System, Santa Clara, California, USA).

#### 3.2 Sample identification

Table 1 lists all the sample identification (ID), sample locations, landfills, abbreviations, and the description of the samples.

Sample ID	Landfill	Sampling point
12P1	BRA	Gas collector from compartment 12, clusterpipe 1
12P2	BRA	Gas collector from compartment 12, clusterpipe 2
1P1	BRA	Gas collector from compartment 11Z, clusterpipe 1
1P2	BRA	Gas collector from compartment 11Z, clusterpipe 2
2P1	BRA	Gas collector from compartment 11Z, clusterpipe 3
2P2	BRA	Gas collector from compartment 11Z, clusterpipe 4
NP1	BRA	Gas collector from compartment 11N, clusterpipe 1
NP2	BRA	Gas collector from compartment 11N, clusterpipe 2
Bulk	BRA	Bulk gas collector
B1, C8, E2	BRA	Gas injection well from compartment 11N
J10, L5, N3, O8	BRA	Gas injection well from compartment 11Z
S6, T3, U5, V3, V8	BRA	Gas injection well from compartment 12
CP1, CP2, CP5	KRA	Gas extraction collector
G26	KRA	Gas extraction well
12, 22, 29, 42, 62, 98, 115, 122	WIE	Gas extraction well
Bulk	WIE	Bulk gas collector
BRA = Braambergen landfi	II, KRA =	Kragge landfill, WIE = Wieringermeer landfill

Table 1. Sample names and the description of the sample sites

#### 3.3 Aeration efficiency

Aeration efficiency (AE) was estimated as an indicator of aerobic processes by relating the concentration of total  $CO_2$  to anaerobic  $CO_2$  and is calculated as (Gebert et al., 2023):

$$AE = \frac{[CO_{2,TOT}] - [CO_{2,AN}]}{[CO_{2,TOT}] + [CH_4]} \times 100$$
(1)

where AE = aeration efficiency (%),  $[CO_{2,TOT}]$  = concentration of total CO<sub>2</sub> (vol.%),  $[CO_{2,AN}]$  = concentration of anaerobically produced CO<sub>2</sub> (vol.%) which is equal to the concentration of CH<sub>4</sub> (vol.%),  $[CH_4]$  = concentration of CH<sub>4</sub> (vol.%).

#### 3.4 Ratio of nitrogen to argon

The main challenge of analysing N<sub>2</sub> originating from landfills is the background N<sub>2</sub> level in the atmosphere that obfuscates the share of N<sub>2</sub> in the total mixture that is impacted by denitrification or nitrogen fixation in the waste. Argon is an inert gas in the atmosphere that can be used as a gas tracer to investigate nitrogen fixation and denitrification (Nagamori et al., 2016; Shigemitsu et al., 2016). Net production of N<sub>2</sub> by denitrification is assumed if the ratio measured in the landfill gas  $\left[\frac{N_2}{Ar}\right]_{Measured}$  exceeds the atmospheric ratio ( $\left[\frac{N_2}{Ar}\right]_{Atm}$ ), while net consumption of N<sub>2</sub> by nitrogen fixation is assumed if the ratio measured in the landfill gas is assumed if the ratio in the landfill gas is lower than the atmospheric ratio [Eq. 2]. In addition, higher  $N_{2, LFG}$  than  $N_{2, atm}$  indicate denitrification due to excess N<sub>2</sub> and lower ratio is assumed to be nitrogen fixation due N<sub>2</sub> loss when compared to atmospheric N<sub>2</sub>/Air ratio [Eq. 4].

$$\frac{N_2}{Ar} = \frac{\left[\frac{N_2}{Ar}\right]Measured}{\left[\frac{N_2}{Ar}\right]Atm}$$
(2)

where N<sub>2</sub> is the measured nitrogen concentration, *Ar* is the measured argon in the sample,  $N_{2,atm}$  is 78.084%, and *Ar<sub>air</sub>* is 0.934% in the atmosphere (National Oceanic and Atmospheric Administration, 2023).

We can then estimate the atmospheric  $N_2$  of the gas sample:

$$N_{2,Atm} = Ar_{measured} \left(\frac{N_{2,Atm}}{Ar_{Atm}}\right)$$
(3)

Subsequently, N<sub>2</sub> produced by or comsumed in the landfill ( $N_{2, LFG}$ ) can be estimated as a % of the total N<sub>2</sub>:

$$N_{2, LFG}(\%) = \frac{N_{2, measured} - N_{2, Atm}}{N_{2, measured}} x \ 100\%$$
(4)

#### 4. RESULTS AND DISCUSSION

The BRA gas samples were separated according to their origin from the three landfill compartments (BRA 11N, BRA 11Z, BRA 12) and the BRA bulk gas. Bulk gas samples reported for BRA and WIE represent the bulk extracted mixture from all compartments. The first section provides information regarding the concentrations of N<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub> and O<sub>2</sub> in the gas from each of the three landfills. The ratio of CO<sub>2</sub> to CH<sub>4</sub> and the aeration efficiency % were used as an indicator of aerobic and anerobic microbial activity. The second section describes the share of N<sub>2</sub> as influenced by the balance between denitrification and nitrogen fixation.

#### 4.1 Composition of landfill gas (N2O, CO2, CH4 and O2)

Figure 1 illustrates the averaged, mean and the distribution of all landfill gases and the expected atmospheric trace gases (shown in red dotted horizontal lines). The highest  $CO_2$  (43%) was found in BRA11Z, but KRA had the highest mean of ~27%  $CO_2$  (Figure 1a). The second highest mean  $CO_2$  concentration (~18.5) was from WIE.

CH<sub>4</sub> concentration was the highest in KRA (~49%) and the aerated pilots (BRA and WIE) had CH<sub>4</sub> a mean ranging from 4 – 10% (Figure 1b). KRA operating with liquid recirculation through the wastes comprising a high share of domestic waste contents showed the highest CH<sub>4</sub> and CO<sub>2</sub> concentration out of all landfills studied. The low CO<sub>2</sub>/CH<sub>4</sub> ratio (< 1) indicates strictly anaerobic microbial activity (Figure 2), as evidenced also by O<sub>2</sub> concentrations < 1.0% (Figure 1f). Argon was the lowest in KRA (~0.3% Ar) compared to other landfills due to lack of atmospheric air present in the landfill waste.

All the gas components in BRA landfills were highly heterogeneous between the compartments.  $CO_2$  concentrations in the BRA between the compartments were not uniform, with the lowest mean  $CO_2$  (~7%) observed in BRA11Z, consistent to a previous work (Meza et al., 2022). The mean  $CO_2$  was ~15 – 16% for all the other aeration pilot landfills (BRA11N, BRA12 and bulk). Figure 1f shows the highest  $O_2$  concentration from BRA11Z (~14%  $O_2$ ) and the lowest  $CO_2/CH_4$  ratio compared to other BRA compartments as high water tables impeded  $O_2$  infiltration and hence consumption into the wastes (Meza et al. 2022; Gebert et al. 2022). All the other compartments (11N, 12, bulk) performed similarly with BRA 12 having the largest data spread. The mean argon concentration between the BRA compartments and WIE were similar (~0.8%) but the concentrations were still slightly lower than the the atmosphere. Higher Ar (near 0.9%) indicates the presence of atmospheric air in the landfill gas.



Figure 1. Gas components in landfill gas from Braambergen (BRA), Kragge (KRA) and Wieringermeer (WIE) landfills evaluated as % of: a) CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, N<sub>2</sub>O, Ar, and O<sub>2</sub>. Three different compartments in BRA are presented as 11N, 11Z, 12, and bulk gas. Box =  $25^{th}$ - $75^{th}$  percentile, line = mean, open symbol = average, whiskers =  $10^{th}$ -

90<sup>th</sup> percentile.

In WIE, the CO<sub>2</sub>/CH<sub>4</sub> ratio was the highest (mean of ~4) compared to all the other all landfills in this study (Figure 2). WIE appears to be at an advanced biodegradation stage suggesting that overextraction is more effective in aerating the waste body than the air injection/extraction mode employed on landfill BRA. However, this aeration also lead to the highest N<sub>2</sub>O concentrations compared to the other landfills in this study (Figure 1d). N<sub>2</sub>O as high as ~20 ppm was detected, with a mean of concentration of ~0.7 ppm. All the other landfills had no N<sub>2</sub>O concentrations, except in E2 well with a 1.7 ppm N<sub>2</sub>O located in BRA11N compartment.

Intensive aeration can cause higher  $N_2O$  concentrations, particularly in nitrifying conditions. Consistent to our observations,  $N_2O$  concentration can be the highest in in-situ aeration treatment systems that are operating dry (Brandstätter et al., 2015). Indeed, landfill WIE shows the lowest water tables and the highest aeration efficiencies compared to the BRA compartments (Gebert et al., 2023).  $N_2O$  is also a by-product of denitrification and other mechanisms (e.g. ammonium oxidation or nitrifier denitrification (Wrage et al., 2001)). Analysis of the microbial community composition in the landfills under study is still ongoing to identify dominant N transformation pathways in the landfills under study.



Figure 2. Ratio of CO<sub>2</sub> to CH<sub>4</sub> from: 1) Braambergen (BRA) bulk gas and the three compartments in BRA (11N, 11Z, 12), 2) Kragge (KRA), and 3) Wieringermeer (WIE) pilot landfills. Box =  $25^{th}-75^{th}$  percentile, line = mean, open symbol = average, whiskers =  $10^{th}-90^{th}$  percentile.

#### 4.2 Aeration efficiency

Equation 1 was used to quanitify the methanotrophic aeration efficiency (AE, Figure 3a) using the fraction of  $CO_2$  in the gas sample and comparing it to the expected ratio of  $CO_2/CH_4$  of 1 (Gebert et al., 2023). The concept assumes  $CO_2$  as the terminal product of aerobically biodegraded organic wastes, thus the ratio of  $CO_2$  to  $CH_4$  in the gas phase can be actualised compared to the ratio in anaerobic condition.

For landfill Braambergen, the compartment with the highest mean effiency was BRA 11N, and as expected from earlier observation of high water tables, BRA 11Z had the lowest aeration efficiency (Meza et al., 2022). Even strictly anaerobic conditions were observed in 11Z, particularly in wells O8, L5 and 1P1. In BRA 12, wells T3 and V3 also had negative aeration efficiencies, indicating anaerobic conditions. It is clear that achieving homogeneous aeration throughout the landfill is a major challenge due to perched water and the heterogeneity and anisotropic nature of landfilled waste, obstructing gas flow (Gebert et

al., 2021; Xu et al., 2020) and leading to the persistence of anaerobic pockets.

WIE exhibited the highest mean aeration efficiency of ~58%, performing the best compared to the other aerated landfill compartments. Over-extraction of air appeared to enhance aeration efficiency more than air injection (BRA). The lower efficiencies (AE < 0%) were also observed at WIE in October and/or in November when the average fall precipitation (~253 mm between 1991-2020) is the highest in the Netherlands and evapotranspiration is already low (KNMI, 2023).

Aeration efficiency were correlated with denitrification as shown in Figure 3c. Aeration can accelerate biowaste degradation and production of nitrate, and thus enhance dentrification rates as shown in BRA and WIE landfills. In low oxygen concentrations, decreased denitrification have been observed in wastewater treatment systems (Oh and Silverstein, 1999) as less nitrate is availables, which is assumed to reflect the situation on the strictly anaerobic landfill de Kragge.



Figure 3. (a) aeration efficiency (%) from equation 1 and excess nitrogen in landfill gas from Braambergen (BRA), Kragge (KRA) and Wieringermeer (WIE) landfills evaluated as (b)  $N_2$ /Ar ratio calculated from equation 2, and (c) % total  $N_2$  calculated from equation 4. Box = 25<sup>th</sup>-75<sup>th</sup> percentile, line = mean, open symbol = average, whiskers = 10<sup>th</sup>-90<sup>th</sup> percentile.

#### 4.2 Ratio of N2 to Ar

Figure 3b shows the ratio of  $N_2$  to Ar measured in the landfill gas over the ratio of  $N_2$  to Ar in atmospheric air, calculated from equation 2 and figure 1b illustrates the excess nitrogen calculated according to equation 4, for all investigated landfills. In BRA, the three compartments showed different behaviour, with the highest excess  $N_2$  in compartment 11N, followed by compartments 11Z, bulk gas (a mixture of all compartments) and compartment 12 (Figure 3c). Because of the large range, the data set was further divided into individual monitoring points, illustrating significant spatial and seasonal differences of excess  $N_2$  concentrations (Figures 4-6). It appears that seasonal variation had a larger impact on  $N_2$  transformation than spatial differences. The balance between all N forming and N consuming processes leads to up to 10% of excess  $N_2$ .

#### De Kragge landfill

In KRA, the ratio of N<sub>2</sub> to Ar in the landfill gas sampled in November 2022 and May 2023 was mostly lower than the atmospheric ratio, leading to negative values for 'excess N<sub>2</sub>', indicating net nitrogen uptake (fixation) except for location CP5 from May (Figure 4). Seasonal effects were predominately observed in BRA and WIE, but less so in KRA where recirculation of treated leachate was used as a means to enhance degradation. It is noteworthy that the data suggest net N uptake despite the fact that the landfill leachate shows  $NH_4^+$  concentrations of ~950 mg/l. The ongoing analysis of the composition of the microbial community should reveal the presence of N fixing microorganisms if this process indeed is relevant.



Figure 4. Mean excess nitrogen concentration (% of the total N<sub>2</sub>) in landfill gas from Kragge (KRA) obtained from equation 4 showing temporal and spatial differences. The blue underlined text indicates sample ID (compare Table 1). Error bars represent standard errors.

#### Braambergen landfill

BRA11Z had the least spatial and temporal variance compared to 11N, 12 and the bulk. BRA 11Z had excess N<sub>2</sub> ranging 2 – 9% N<sub>2</sub> of the total N<sub>2</sub> over spatial distance and time, and BRA 11N had a higher variability than BRA 11Z because of two samples (NP1 and NP2) with excess landfill N<sub>2</sub> ranging between 1 - 12% N<sub>2</sub>. (Figure 5a & b). BRA 12 had N<sub>2</sub> concentrations similar to 11N but excess N<sub>2</sub> ranged between -2% (in winter) to as high as 11% in the summer (Figure 5c). Two samples in compartment 12 (12P2 and

well T3) had lower N<sub>2</sub> than atmospheric, suggesting an occurrence of N<sub>2</sub> fixation. Nevertheless, the range of N<sub>2</sub>% excess was similar for the compartments despite having different waste sources, different water levels (Meza et al., 2022), and different aeration efficiencies (Figure 3a).

Seasonal differences were also observed as shown in the BRA bulk samples (Figure 5d), the % excess N was >0. In fact, BRA 11N and BRA 12 exhibited similar seasonal pattern as BRA bulk showing higher N<sub>2</sub> concentrations in warmer months. Gebert et al (2023) illustrated higher aeration efficiencies in the summer months, likely due to lower moisture of the cover soil. Higher aeration efficiency would enhance nitrification and hene the nitrate available for further denitrification.

The results clearly indicate heterogeneous excess  $N_2$  concentrations despite applying the same aeration treatment regime over the three BRA compartments. Possible reasons could be heterogeneity regarding: 1) waste source and hence N composition and ensuing metabolic pathways, 2) intrinsic permeability of wastes (Xu et al., 2020) and hence regarding gas/air transport properties and resulting differences in aeration efficiency (Meza et al., 2022), and 3) water distribution in the wastes (Gebert et al., 2022). In summary, different processes can occur simultaneously that can influence  $N_2$  production from the three compartments on the aeration pilot Braambergen.



Figure 5. Mean excess nitrogen concentration (% of the total  $N_2$ ) in landfill gas calculated using equation 4 from Braambergen (BRA) compartment 11Z, 11ZN, 12, and bulk gases showing spatial and temporal differences. The blue underlined text indicates sample ID (compare Table 1). Error bars represent standard errors.

#### Wieringermeer landfill

Wieringermeer landfill is operated by over-extracting landfill gas through the wells to produce negative pressure within the landfill to allow atmospheric air to intrude into the waste body. Here, similar levels of excess  $N_2$  as in the BRA compartments (Figure 6) were measured. However, higher  $CO_2/CH_4$  ratio and higher aeration efficiency were observed in WIE than BRA compartments. This suggests more  $O_2$  intruded into the waste body as the terminal electron acceptor to be available for microorganisms (Figure 2),

resulting in a higher share of  $CO_2$  in the final gas mixture. Excess  $N_2$  also showed similar seasonal trends to landfill BRA. Excess  $N_2$ % decreased in colder months and increased in warmer months with higher net denitrification occurring mostly in August when temperatures are warmer and lower net denitrification in winter months.

The net positive values for excess  $N_2$  in the aerated sites suggests that aeration enabled conditions for denitrification, leading to net release of nitrogen via the gas phase. Anammox can also produce landfill  $N_2$ , but this process occurs in anaerobic ammonium oxidation conditions. With BRA and WIE operating either by  $O_2$  injection or  $O_2$  intrusion via negative pressure, denitrification was the dominating process for both BRA and WIE, with the exception of very few data points.

Landfill aeration through air intrusion or gas well over-extraction can be inefficient and not oxygenate an entire landfill sufficiently. This means that anaerobic regions will persist in the landfill due to  $O_2$ transport limitation or because  $O_2$  is rapidly consumed, which can then change oxygenated regions to turn anaerobic. In both cases, nitrate can first be produced by nitrification under aerobic conditions and then used for anammox or by denitrification.



Figure 6. Mean excess nitrogen concentration in landfill gas from Wieringermeer (WIE) showing spatial and temporal differences. The blue underlined text indicates sample ID (compare Table 1). Error bars represent standard errors.

The %N<sub>2</sub> excess reported in this study were consistent to previous work that explored nitrogen transformation in batch reactors (Brandstätter et al., 2015). Brandstätter et al. (2015) employed three batch reactor types to simulate landfill operations in duplicate: 1) aerated with water addition and recirculation (aerated wet), 2) operated without water addition (aerated dry), and 3) recirculated water to promote anaerobic conditions (wet). Aerated wet conditions from the batch experiments had 15.4 – 16.6% N<sub>2</sub> concentrations out of the total nitrogen inside the batch reactor, aerated dry process released 2.6 – 8.8% N<sub>2</sub>, and the wet conditions emitted 4 – 6.2% N<sub>2</sub> based on % initial total nitrogen. It was concluded that different water quantities in the landfill and the in-situ aeration regimes can impact nitrogen transformation.

#### 5. CONCLUSIONS AND OUTLOOK

In this study, we compared the ratio of  $N_2$  to Ar in landfill gas to the atmospheric ratio to determine the balance between N fixation and denitrification and thereby quantify net nitrogen uptake and net nitrogen loss for three landfills under full-scale in-situ stabilisation. Up to 13% of the  $N_2$  could be explained by the net dominating effect of denitrification in the landfills under in situ aeration, while in the landfill under recirculation up to 17% of  $N_2$  in the landfill gas were gained through the net dominating effect of N fixation. The data appear consistent with previous studies that explored nitrogen concentrations from landfills under different aeration regimes and also consistent with a study that suggested recirculation in batch landfill reactors to produce less excess  $N_2$  than in aerated conditions. Further work is needed to understand the effects of liquid recirculation on N dynamics.

In the future, the composition of the microbial community responsible for N-transformations will be analysed to underpin our understanding of the dynamics of nitrogen removal via the gaseous phase. Gas flow rates will be used to quantify the amount of nitrogen resulting from the balance of denitrification and N fixation in absolute terms.

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#### REFERENCES

- Brand, E., de Nijs, T., Claessens, J., Dijkstra, J.J., Comans, R.N.J., Lieste, R., 2014. Development of emission testing values to assess sustainable landfill management on pilot landfills. Phase 2 : Proposals for testing values 171.
- Brandstätter, C., Laner, D., Fellner, J., 2015. Nitrogen pools and flows during lab-scale degradation of old landfilled waste under different oxygen and water regimes. Biodegradation 26, 399–414. https://doi.org/10.1007/s10532-015-9742-5
- Chu, Y.-X., Wang, J., Jiang, L., Tian, G., He, R., 2022. Intermittent aeration reducing N2O emissions from bioreactor landfills with gas–water joint regulation. Waste Manag. 139, 309–320. https://doi.org/https://doi.org/10.1016/j.wasman.2021.12.041
- Cruz, C., Lammen, H., Oonk, H., 2021. Sustainable landfill management: carbon removal in two aerated landfills., in: Sardinia 2021 18th International Symposium on Waste Management and Sustainable Landfilling.
- Gebert, J., Jong, T. De, Rees-white, T., Beaven, R., Lammen, H., 2021. Spatial Variability of Leachate Tables , Leachate Composition and Hydraulic Conductivity in a Landfill Stabilized By in Situ Aeration.
- Gebert, J., Meza, N., Cruz, C., Lammen, H., 2023. Assessing efficiency of landfill aeration by full scale carbon mass balancing, in: Sardinia 2023, 19th International Symposium on Landfill Management and Sustainable Landfilling.
- Harborth, P., Fuß, R., Münnich, K., Flessa, H., Fricke, K., 2013. Spatial variability of nitrous oxide and methane emissions from an MBT landfill in operation: Strong N2O hotspots at the working face. Waste Manag. 33, 2099– 2107. https://doi.org/10.1016/J.WASMAN.2013.01.028
- iDS, n.d. Introductie Duurzaam Stortbeheer [WWW Document]. URL https://duurzaamstortbeheer.nl/
- KNMI, 2023. Klimaat van Nederland Climate Dashboard: De Bilt Fall precipitation amount from 1991-2020 [WWW Document]. K. Ned. Meteorol. Instituut, Minist. van Infrastuct. en Waterstaat. URL https://www.knmi.nl/home (accessed 6.29.23).
- Lammen, H., Cruz, C., Scharff, H., 2021. Sustainable Landfill Management : Leachate Development in Two Aerated Landfills, in: Sardinia 2021 18th International Symposium on Waste Management and Sustainable Landfilling.

- Li, W., Sun, Y., Bian, R., Wang, H., Zhang, D., 2017a. N2O emissions from an intermittently aerated semi-aerobic aged refuse bioreactor: Combined effect of COD and NH4+-N in influent leachate. Waste Manag. 69, 242–249. https://doi.org/10.1016/J.WASMAN.2017.08.022
- Li, W., Sun, Y., Li, G., Liu, Z., Wang, H., Zhang, D., 2017b. Contributions of nitrification and denitrification to N2O emissions from aged refuse bioreactor at different feeding loads of ammonia substrates. Waste Manag. 68, 319– 328. https://doi.org/10.1016/J.WASMAN.2017.06.037
- Meza, N., Lammen, H., Cruz, C., Heimovaara, T., Gebert, J., 2022. Spatial Variability of Gas Composition and Flow in a Landfill Under in-Situ Aeration. Detritus 19, 104–113. https://doi.org/10.31025/2611-4135/2022.15191
- Nagamori, M., Mowjood, M.I.M., Watanabe, Y., Isobe, Y., Ishigaki, T., Kawamoto, K., 2016. Characterization of temporal variations in landfill gas components inside an open solid waste dump site in Sri Lanka. J. Air Waste Manag. Assoc. 66, 1257–1267. https://doi.org/10.1080/10962247.2016.1212746
- National Oceanic and Atmospheric Administration, 2023. Atmosphere: Introduction to the atmosphere, US Department of Commerce.
- NWO, 2019. Coupled multi-process research for reducing landfill emissions (CURE) [WWW Document]. URL https://www.nwo.nl/en/projects/ocenwgroot2019092 (accessed 6.26.23).
- Oh, J., Silverstein, J., 1999. Oxygen inhibition of activated sludge denitrification. Water Res. 33, 1925–1937. https://doi.org/10.1016/S0043-1354(98)00365-0
- Shigemitsu, M., Gruber, N., Oka, A., Yamanaka, Y., 2016. Potential use of the N<sub>2</sub>/Ar ratio as a constraint on the oceanic fixed nitrogen loss. Global Biogeochem. Cycles 30, 576–594. https://doi.org/10.1002/2015gb005297
- Sun, Y., Wang, Y.N., Sun, X., Wu, H., Zhang, H., 2013. Production characteristics of N2O during stabilization of municipal solid waste in an intermittent aerated semi-aerobic bioreactor landfill. Waste Manag. 33, 2729–2736. https://doi.org/10.1016/J.WASMAN.2013.08.013
- Wrage, N., Velthof, G.L., van Beusichem, M.L., Oenema, O., 2001. Role of nitrifier denitrification in the production of nitrous oxide. Soil Biol. Biochem. 33, 1723–1732. https://doi.org/https://doi.org/10.1016/S0038-0717(01)00096-7
- Xu, X.B., Powrie, W., Zhang, W.J., Holmes, D.S., Xu, H., Beaven, R., 2020. Experimental study of the intrinsic permeability of municipal solid waste. Waste Manag. 102, 304–311. https://doi.org/10.1016/j.wasman.2019.10.039
- Zhang, H., He, P., Shao, L., 2009. N2O emissions at municipal solid waste landfill sites: Effects of CH4 emissions and cover soil. Atmos. Environ. 43, 2623–2631. https://doi.org/https://doi.org/10.1016/j.atmosenv.2009.02.011