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Cd, Cr, and Pb concentrations increase in maturing compost while the metal inventory does not: implications for compliance sampling and digestion protocols

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Abstract

Compost compliance monitoring assumes that the trace-metal content of a maturing pile is a stable measurable quantity, and co-composting poultry litter (PL) with a low-metal bulking agent is promoted on that basis. That assumption is rarely tested. We tracked eight elements (Zn, Cu, Fe, Mn, Ni, Cr, Cd, Pb) through a 90-day pit composting cycle at five PL: vegetable waste (VW) ratios. Measured Cd in the pure-PL pile rose from 0.84 to 3.34 mg kg⁻¹, but nothing adds metal to a closed pile: non-volatile mass is conserved, so a concentration change must come from dry-matter loss or from a change in the fraction recovered by the digestion. A mass-conservative partition model separates them as a liberation factor, Λ . Zn, Cu, Mn and Ni behaved conservatively ($\Lambda = 1.03$) whereas Cr, Cd and Pb required $\Lambda = 5.11$ (95% CI 3.05–8.23), separating even when dry-matter loss was forced to 50%. Mineral ingress, bounded at 0.13% w/w by Fe, explains at most 4% of it; liberation followed first-order kinetics ($t_{1/2} = 49$ d). The increase therefore records rising recovery from a humifying matrix, not accumulation, and the compliance verdict for one unchanged pile inverts within the cycle: compliant at 15 days, 2.2 times the EU Cd limit at 90 days. Compliance sampling should be tied to an independent maturity criterion and protocols should specify a near-total digestion; here, the exceedance risk for the Cd limit reaches 5% at a PL share of 37%.

Keywords Compliance monitoring · Sampling design · Pseudo-total digestion · Cadmium · Co-composting · Dietary exposure

1 Introduction

Intensive poultry production generates litter faster than safe recycling routes have developed for it, particularly across South Asia. Poultry litter (PL) is a concentrated source of nitrogen (N) and phosphorus and an attractive substitute for mineral fertilizer, but it also accumulates trace metals derived from the feed chain. Zinc (Zn) and copper (Cu) are administered deliberately as growth promoters and gut-health agents and are excreted almost quantitatively; cadmium (Cd), chromium (Cr) and lead (Pb) enter incidentally as impurities in phosphate supplements and mineral premixes (Nicholson et al., 1999; Bolan et al., 2010). Direct land application of raw PL therefore transfers a metal burden to soil alongside the nutrients, and repeated application concentrates that burden in the plow layer, where Cd in particular is mobile enough to enter the human food chain through cereal and vegetable uptake (Woodbury, 1992; Smith, 2009; Kabata-Pendias, 2011).

Composting is the conventional stabilization route. Co-composting, the blending of PL with a low-metal, high-carbon bulking agent, is advocated both to improve the physical structure and C:N ratio of the pile and to dilute its metal content (Bernal et al., 2009). Market vegetable waste (VW) is an appealing bulking agent in urban South Asia: it is abundant, free at the point of collection, and otherwise landfilled. Two questions follow, and neither has a satisfactory quantitative answer for these feedstocks.

42 The first is practical. **How much dilution is required?** Statutory contaminant ceilings for compost differ by more than an
43 order of magnitude between jurisdictions. Regulation (EU) 2019/1009 caps Cd in Component Material Category 3
44 compost at 1.5 mg kg⁻¹ dry matter, whereas the corresponding “pollutant concentration” ceiling under 40 CFR 503.13 sits
45 at 39 mg kg⁻¹ (European Parliament and Council, 2019; US Environmental Protection Agency, 1993). The blending ratio
46 needed for compliance is therefore jurisdiction-specific, and it has rarely been derived empirically with any statement of
47 the residual risk attaching to a given choice.

48 The second question is more fundamental, and is the subject of this paper. **Is the metal content of a composting pile a**
49 **stable measurable quantity at all?** Under aerobic composting, trace metals other than mercury are not volatilized, so
50 their total mass within a closed pile is conserved. Measured concentrations nonetheless rise, because organic matter (OM)
51 mineralizes and the matrix shrinks. This “concentration effect” is thoroughly documented and is routinely invoked to
52 explain increases of 20–60% over a composting cycle, a range that corresponds closely to the 20–40% dry-matter losses
53 typical of turned windrows (Paré et al., 1998; Hsu & Lo, 2001; Bernal et al., 2009).

54 What is far less often examined is whether observed increases actually *fit* that explanation quantitatively. The mass-loss
55 argument makes a hard, falsifiable prediction. If metals are conservative and matrix loss is the only process operating, then
56 **every** element in the pile must enrich by the **same** factor, $1/(1 - L)$, where L is the fractional dry-matter loss. Elements that
57 enrich appreciably more than this cannot be explained by mass loss; and elements that diverge from one another within the
58 same pile cannot all be behaving conservatively. The test is simple; it requires no additional measurement, and it converts
59 a qualitative appeal to the concentration effect into a quantitative constraint. Mass and element balances have been
60 reported for composting systems, and the method dependence of compost digestion is documented (Hseu, 2004); what has
61 not been done, to our knowledge, is to combine the two: to use the within-suite divergence between elements as an internal
62 control on whether the concentration effect can account for the observed changes at all, and to resolve the residual as an
63 explicit, time-resolved quantity.

64 There is good reason to expect the test to fail for some elements. Strong-acid digestions of the kind used almost universally
65 in compost analysis (nitric–perchloric, nitric–hydrochloric, or microwave-assisted variants) recover a *pseudo-total* rather
66 than a true total metal content. Their recovery is matrix-dependent: metal occluded within lignocellulosic structures, or
67 bound in refractory mineral inclusions, is incompletely attacked, and the reported content of a given compost can differ
68 substantially between digestion procedures (Hseu, 2004). Composting fundamentally alters that matrix. Lignocellulose is
69 depolymerized, and the residue converts to humic substances rich in carboxyl and phenolic functional groups that bind
70 metals in readily acid-extractable forms. Sequential-extraction studies of composting sludges and manures consistently
71 report large redistributions between operational fractions during maturation, with the exchangeable and organically bound
72 pools growing at the expense of the residual pool (Liu et al., 2007; He et al., 2009; Amir et al., 2005; Zheng et al., 2007).
73 If the residual pool is the one a pseudo-total digestion under-recovers, then measured concentration should rise with
74 maturity even when the metal inventory is fixed.

75 Here we bring these threads together. We track eight elements through a 90-day co-composting cycle across five PL: VW
76 ratios and interrogate the resulting matrix with an explicit mass-conservative partition model. Specifically, we (i) quantify
77 how the blending ratio controls the final metal load; (ii) partition every observed concentration change into a matrix-loss
78 term and a liberation term, and test whether the liberation term is distinguishable from zero; (iii) establish the robustness of
79 that partition across the entire physically plausible range of dry-matter loss; (iv) test and reject mineral ingress as an
80 alternative explanation using iron (Fe) as an internal tracer; (v) characterize the kinetics of liberation; and (vi) translate the
81 findings into compliance probabilities, ecological risk indices and long-term soil-accumulation trajectories. The central
82 result is that three toxicologically important elements, Cd, Cr, and Pb, fail the conservation test decisively, with direct
83 consequences for how and when compost compliance samples should be taken.

84 Four contributions follow, and none of them is a model output. The first is a diagnostic rather than a result: the divergence
85 test needs no measurement beyond a multi-element dataset that most composting laboratories already hold, so it can be
86 applied retrospectively to published series to ask whether their reported increases are consistent with mass loss at all. The
87 second is a reinterpretation of an existing literature: sequential-extraction studies have long reported metal moving out of
88 the residual fraction during maturation and have read this as a change in speciation, but if the residual fraction is the one a
89 pseudo-total digestion under-recovers, then the same redistribution must also inflate the apparent total, and speciation
90 change and total-content change become two readings of one process. The third is a specific and remediable failure mode
91 in compost regulation, in which the compliance verdict on an unchanged pile depends on when it was sampled and how

aggressively it was digested. The fourth is a cheap internal control: in an unlined system, Fe bounds mineral ingress and so converts an untestable assumption into a quantity with an upper limit.

2 Materials and methods

2.1 Feedstocks, treatments and composting procedure

The composting trial was carried out in 2009 at the research area of PMAS–Arid Agriculture University, Rawalpindi, Pakistan (33.6° N, 73.1° E, 508 m a.s.l.), in a semi-arid subtropical climate with an annual mean precipitation of approximately 1000 mm. PL was collected from private broiler sheds within the district; it comprised excreta together with wheat-straw and rice-husk bedding. VW was collected from the municipal wholesale vegetable market and consisted predominantly of leaf, stalk, and trimming residues from brassicas, cucurbits, and alliums.

Five treatments were established as PL: VW mass ratios of 100:0 (T1), 75:25 (T2), 50:50 (T3), 25:75 (T4), and 0:100 (T5). Each treatment occupied an unlined earthen pit of $1.22 \times 1.22 \times 0.61$ m (L $\times$ W $\times$ D). Feedstocks were shredded, weighed to the target ratio, mixed, and charged to the pits. Piles were composted under ambient conditions and were turned and remixed once, on day 20, to re-aerate the profile and homogenize the wall and core material. Selected properties of the mature products are given in Table 1.

Table 1 Composition of the five feedstock blends and selected properties of the mature composts.

Treatment	PL (% w/w)	VW (% w/w)	pH ^a	EC ^a (dS m ⁻¹)	C:N ^a
T1	100	0	7.35	5.26	14.87
T2	75	25	7.30	7.00	14.50
T3	50	50	6.91	9.68	13.91
T4	25	75	6.62	10.84	13.72
T5	0	100	6.25	11.50	13.23

PL, poultry litter; VW, vegetable waste; EC, electrical conductivity; C:N, ratio of organic carbon to total N. The five blends are identified as T1–T5 throughout. ^a Determined on the day-90 product; pH and EC in a 1:5 (w/v) aqueous extract.

Part of the primary concentration dataset has been reported in an institutional thesis (Manzoor, 2010). The modeling framework, the partition analysis, the kinetic treatment, the compliance and risk models, and all conclusions presented here are new to this paper.

2.2 Sampling scheme and analytical procedures

Piles were sampled at 15, 30, 45, 60, 75 and 90 days after charging. On each occasion, three composite samples were drawn per pit, each composite being formed from five sub-samples taken at different depths and horizontal positions and homogenized by quartering. Samples were air-dried, oven-dried at 65 °C to constant mass, ground to pass a 0.5 mm sieve and stored in sealed polyethylene containers.

Organic carbon was determined by loss on ignition in a muffle furnace at 500 °C for 2–4 h and calculated as C (%) = (100 – ash %)/1.8. Total N was determined colorimetrically at 655 nm following digestion in a hydrogen peroxide–lithium sulfate–selenium mixture at 360 °C (Anderson & Ingram, 1993). pH and electrical conductivity were measured in 1:5 (w/v) aqueous extracts.

For elemental analysis, 1.0 g of ground material was digested in 10 mL of nitric acid: perchloric acid (2:1, v/v), left to stand overnight, then heated in a block digester to 235 °C until dense white perchloric fumes appeared; digests were cooled and made to 100 mL with deionized water (Isaac & Johnson, 1975). Zn, Cu, Fe, manganese (Mn), nickel (Ni), Cr, Cd and Pb were quantified by flame atomic absorption spectrometry against matrix-matched standards, with reagent blanks carried through the full procedure.

We emphasize throughout that a nitric–perchloric digest yields a **pseudo-total** metal content. It dissolves exchangeable, carbonate-bound, organically complexed and oxide-associated fractions and much, but not all, of the silicate-occluded

residue; its recovery is matrix-dependent. Hseu (2004) compared four digestion procedures across nine composts and found that nitric-perchloric digestion recovered less Cd, Mn and Ni than nitric acid alone, confirming that the reported value depends on both the method and the matrix. It is not an operational measure of bioavailability, and that term is avoided here.

2.3 Analytical quality control and its limits

Because the central argument of this paper concerns analytical recovery, the quality controls that were and were not applied are set out in full rather than summarized.

What is documented. The digestion followed the collaborative-study procedure of Isaac and Johnson (1975) rather than a locally devised method, so the protocol is traceable to a published and independently evaluated source. Reagent blanks were carried through the complete procedure in every batch and subtracted. Calibration used matrix-matched standards prepared in the same acid medium as the digests. Every element was determined in the same digest, so instrumental and digestion conditions were common to all eight within a sample.

What can be recovered. Precision is quantifiable from the archived analysis-of-variance tables. Dividing the square root of each error mean square by the corresponding grand mean gives the within-occasion coefficient of variation (CV) for every element at each sampling date; for Cr and Cd the coefficients were tabulated directly in the original record. These are reported in full in Supplementary Table S2. Precision and a validated error term are not the same thing: the tabulated coefficients for Cr and Cd could not be reconciled with the treatment sums of squares by the test described in Sect. 2.4, so they are reported here as precision but were not used to attach standard errors to those means. Median values were 1.5% for Fe, 3.1% for Mn, 5.0% for Ni, 6.4% for Cu, 10.8% for Zn, 1.2% for Cr and 1.4% for Cd, with occasional much larger values that are identified individually in that table. No precision figure of any kind is available for Pb.

What is not available. No certified reference material was analyzed alongside the samples, no record survives of the spectrometer model or of the calibration curves, and the grade and supplier of the acids are not documented. Recovery and therefore trueness cannot be established retrospectively, and we make no claim about the absolute accuracy of the concentrations reported here.

Two considerations bound the effect of that gap on the conclusions. The central claim concerns a change in recovery over time within one laboratory, one method and one instrument, which is a relative comparison; trueness against a reference material would bear on the absolute concentrations, which the argument does not rest upon. And because all eight elements were determined in the same digest, any variation in digestion or instrument response is common to them and cancels in the between-element contrast that carries the result, as quantified in Sect. 4.2. Readers who require certified accuracy for the absolute values should treat them as indicative; the behavioral contrast between element classes does not depend on them.

2.4 Data structure and recovery of error terms

The design was balanced with five treatments, six sampling occasions and three composite samples per pit per occasion. Error mean squares from the analysis of variance were used to derive the standard error of each treatment mean,

$$SE = \sqrt{MS_{\text{error}}/r}, \quad r = 3 \quad (1)$$

Each error term was validated before use. For a balanced design, the treatment sum of squares is exactly reconstructible from the reported means,

$$SS_{\text{treat}} = r \sum_{i=1}^t (\bar{x}_i - \bar{x})^2 \quad (2)$$

and each error mean square admits a second, independent derivation from the reported CV,

$$MS_{\text{error}} = \left(\frac{CV \bar{x}}{100} \right)^2 \quad (3)$$

An error term was accepted only where both checks agreed to within 3%. For Cu, Mn and Ni the sum of squares reconstructed by Eq. (2) did not match the appendix printed under the corresponding sampling day, but matched another day's appendix exactly; the day labels on those tables are transposed in the archived record, and the error terms were reassigned to the occasions their sums of squares identify before being used. For Cu the reassignment is confirmed

independently by Eq. (3), since the tabulated CV for 30 days is reproduced only by the error mean square printed under 45 days and vice versa. The supplementary data file carries both the printed and the corrected mapping so that the reassignment is auditable. Validated error terms were obtained for Zn, Cu, Fe, Mn and Ni. For Cr, Cd and Pb the two derivations could not be reconciled, and those elements are therefore reported as means without error terms; the conclusions drawn for them rest on effect magnitude rather than on formal significance testing (see Sect. 4.7). Standard errors for the validated elements are given in Supplementary Table S1.

2.5 A mass-conservative partition model for metal behavior

Under aerobic composting, the elements considered here are non-volatile, so the total mass M of each element within a pile is conserved. The measured pseudo-total concentration is

$$C(t) = \frac{M f(t)}{m(t)} \quad (4)$$

where $m(t)$ is the dry mass of the pile and $f(t)$ is the fraction of the metal inventory recovered by the digestion. Dry-matter loss is modeled as a first-order process with rate constant λ ,

$$m(t) = m_0 e^{-\lambda t} \quad (5)$$

so that, normalizing to the first sampling occasion t_0 and writing $\Delta t = t - t_0$,

$$\frac{C(t)}{C(t_0)} = \Lambda(t) e^{\lambda \Delta t}, \quad \Lambda(t) = \frac{f(t)}{f(t_0)} \quad (6)$$

Λ is the **liberation factor**: the component of the concentration change that matrix loss cannot account for. Rearranging Eq. (6) gives it explicitly,

$$\Lambda(t) = \frac{C(t)}{C(t_0)} e^{-\lambda \Delta t} \quad (7)$$

$\Lambda = 1$ denotes fully conservative behavior, in which the entire concentration rise is a shrinking-matrix artifact. $\Lambda > 1$ requires that metal inaccessible to the digestion at t_0 has become accessible. Because $f(t) \leq 1$ by definition, a lower bound on θ_0 , the fraction of the inventory unrecovered at the first sampling, follows directly:

$$\theta_0 \geq 1 - \frac{1}{\Lambda} \quad (8)$$

Equation (7) is exact once λ is specified, and requires no curve fitting. However, λ cannot be identified from concentration data alone, and dry-matter loss was not measured gravimetrically. We therefore treat λ as a controlled parameter and evaluate Λ under three scenarios spanning the full plausible range: (S1) a tracer-based estimate in which the two most temporally stable elements are assumed conservative, giving λ from their mean enrichment; (S2) λ fixed to give 30% dry-matter loss over the sampling window; and (S3) λ fixed to give 50% loss, an upper bound for turned windrow composting (Bernal et al., 2009). Fe is excluded from the tracer set on independent grounds established in Sect. 3.1.

For a strictly conservative element ($\Lambda = 1$), the attainable enrichment is bounded by the dry-matter loss alone,

$$EF_{\max} = \frac{C(t)}{C(t_0)} \Big|_{\Lambda=1} = \frac{1}{1-L}, \quad L = 1 - e^{-\lambda \Delta t} \quad (9)$$

which defines the mass-loss ceiling used in Sect. 3.3. The conservative elements also bound λ from above, since $\Lambda < 1$ is physically impossible for an element that is fully recovered at t_0 . This provides an internal consistency check on the scenarios.

2.6 Kinetic description of the liberation process

Where $\Lambda > 1$, its trajectory was described by a first-order approach to an asymptote,

$$\Lambda(t) = \Lambda_{\infty} - (\Lambda_{\infty} - 1)e^{-k \Delta t} \quad (10)$$

with Λ_{∞} the ultimate liberation ratio and k the liberation rate constant. Parameters were estimated by least squares over a dense two-dimensional grid (500×320 nodes); the liberation half-time is

$$t_{1/2} = \frac{\ln 2}{k} \quad (11)$$

Equation (10) was fitted under scenario S2, the mid-range mass-loss assumption. Cu and Ni were fitted as null controls.

2.7 Compliance, ecological risk and soil-accumulation models

Regulatory benchmarks. Mature-product concentrations were compared against Regulation (EU) 2019/1009. Two sets of ceilings bear on a compost placed on the market as a soil improver. Annex II, Component Material Category 3, governs the compost as an input material and limits Cd to 1.5, Ni to 50, and Pb to 120 mg kg⁻¹ dry matter; Annex I, Product Function Category 3(A), governs the finished organic soil improver and limits Cu to 300 and Zn to 800 mg kg⁻¹ dry matter. Both set a Cd ceiling, and the stricter Component Material Category 3 value of 1.5 mg kg⁻¹ is therefore the binding one. Concentrations were also compared against the “pollutant concentration” limits of 40 CFR 503.13 (Cd 39, Ni 420, Pb 300, Cu 1500, Zn 2800 mg kg⁻¹). Both EU annexes set their Cr ceiling on Cr(VI), whereas total Cr was determined here, so Cr is not assessed for compliance.

Monte-Carlo compliance model. The probability that a blend of arbitrary composition breaches the Cd limit was obtained by propagating both regression and analytical uncertainty. Cd concentration was regressed on the PL mass fraction f_{PL} , and 2×10^5 realizations were drawn at each of 201 values of f_{PL} . Because the intercept and slope of an ordinary least-squares fit are correlated, strongly so here at $r = -0.82$, they were not drawn independently. The regression component was instead drawn from the sampling distribution of the fitted mean at each inclusion rate, whose standard error, s times the square root of $[1/n + (f_{PL} - \text{mean } f_{PL})^2/S_{xx}]$, already carries that covariance, where s is the residual standard deviation of the regression, $n = 5$, and S_{xx} is the sum of squared deviations of f_{PL} about its mean. A multiplicative analytical error with CV = 20.8%, the largest CV reported for Cd anywhere in this dataset, was then applied. The exceedance probability is the proportion of realizations above 1.5 mg kg⁻¹.

Geochemical indices. Contamination factors were computed against world mean soil concentrations (Kabata-Pendias, 2011),

$$CF_j = \frac{C_{j, \text{compost}}}{C_{j, \text{background}}} \quad (12)$$

the geoaccumulation index after Müller (1969),

$$I_{\text{geo}, j} = \log_2 \left(\frac{CF_j}{1.5} \right) \quad (13)$$

the pollution load index as the geometric mean of CF over the $n = 6$ regulated pollutants (Tomlinson et al., 1980),

$$PLI = \left(\prod_{j=1}^n CF_j \right)^{1/n} \quad (14)$$

and the potential ecological risk index after Hakanson (1980),

$$RI = \sum_{j=1}^n T_{r, j} CF_j \quad (15)$$

with toxic-response factors T_r of 30 (Cd), 5 (Cu, Ni, Pb), 2 (Cr) and 1 (Zn).

Soil accumulation. Repeated surface application was modeled for a 0–20 cm plow layer of bulk density 1.3 Mg m⁻³, equivalent to $M_{\text{soil}} = 2600 \text{ Mg ha}^{-1}$. For an application rate A (Mg ha⁻¹ yr⁻¹), the annual increment and the interval to reach a target soil concentration are

$$\Delta C = \frac{A C_{\text{compost}}}{M_{\text{soil}}}, \quad \tau = \frac{C_{\text{limit}} - C_{\text{background}}}{\Delta C} \quad (16)$$

evaluated from a background of 0.41 mg kg⁻¹ Cd to the 1.0 mg kg⁻¹ limit of Council Directive 86/278/EEC for soils of pH 6–7 (Council of the European Communities, 1986). Application rates of 5, 10 and 20 Mg ha⁻¹ yr⁻¹ were evaluated; because the interval to a given soil concentration is exactly inversely proportional to the rate, results are tabulated at 10 Mg ha⁻¹ yr⁻¹ and scale directly. The model deliberately omits leaching, plant offtake and erosion, and therefore returns a conservative upper bound on the time to limit.

2.8 Statistical analysis

Group contrasts for enrichment and liberation used the Mann–Whitney U test with tie correction. The natural unit for that test is the element $\times$ treatment combination, but each element contributes one value to every treatment, so units are not mutually independent. The contrast was therefore run at two levels of aggregation: over all element $\times$ treatment units, and over element means, the latter yielding fully independent units at the cost of a much smaller sample. Probabilities are from the normal approximation with tie correction, which at these sample sizes is conservative relative to the exact permutation distribution. Dose–response relationships were fitted by ordinary least squares, and Student t tail probabilities were evaluated from the regularized incomplete beta function and validated against tabulated critical values. Because one such regression was fitted for each of the eight elements, the resulting probabilities were adjusted for multiple testing by the Holm–Bonferroni procedure.

Because the trajectories comprise only six sampling occasions and no replicate-level error term could be validated for Cr, Cd and Pb (Sect. 2.4), the evidence for liberation was additionally assessed by information-theoretic model comparison, which does not depend on a significance threshold. For every element $\times$ treatment series, the liberation model of Eq. (10) was compared against the conservative null $\Lambda(t) = 1$, in which the entire concentration rise is attributed to matrix shrinkage. Support was quantified by the small-sample corrected Akaike information criterion,

$$AIC_c = n \ln \left(\frac{RSS}{n} \right) + 2K + \frac{2K(K+1)}{n-K-1} \quad (17)$$

where RSS is the residual sum of squares and n the number of observations in the series, with $K = 1$ for the null and $K = 3$ for the liberation model (two parameters plus the residual variance), and by the Akaike weight of the liberation model, $w = [1 + \exp(\Delta AIC_c/2)]^{-1}$. Differences of $\Delta AIC_c < -4$ were treated as strong support (Burnham & Anderson, 2002).

Confidence intervals for the group mean liberation factor were obtained by non-parametric bootstrap (20 000 resamples) over element $\times$ treatment units within each group, an approach that requires no assumption about the partly unavailable analytical error.

The correlation structure of the mature products was examined by Spearman rank correlation, which is robust at $n = 5$, and summarized by principal component analysis of the standardized 90-day composition using the eigendecomposition of the correlation matrix. Given the sample size, the ordination is treated as descriptive rather than inferential.

Analyses were implemented in Python 3.11 with NumPy, and the figures drawn with Matplotlib. The digitized dataset and the analysis code are provided as supplementary material, so that every result reported here can be reproduced from the source data.

3 Results

3.1 Blending ratio controls metal load, and Fe marks mineral input

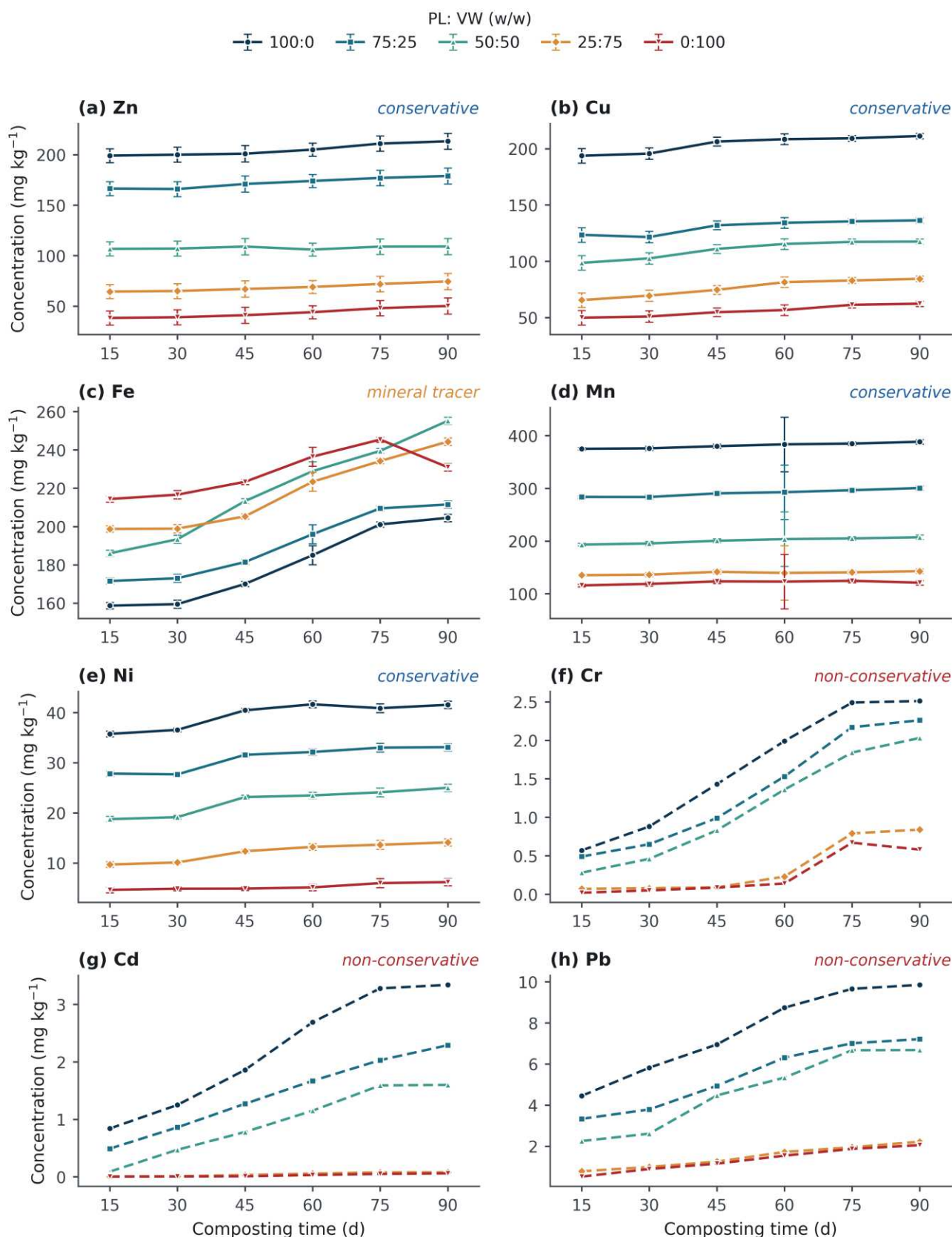
Concentration trajectories for all eight elements are shown in Fig. 1, and mature-product concentrations with their dose–response regressions in Table 2. Seven of the eight elements scaled linearly and strongly with the PL mass fraction. Ni was almost perfectly linear ($r = +0.999$, $P < 0.001$), followed by Zn ($r = +0.985$, $P = 0.002$), Mn ($r = +0.979$, $P = 0.004$), Cd ($r = +0.974$, $P = 0.005$), Cu ($r = +0.964$, $P = 0.008$), Pb ($r = +0.962$, $P = 0.009$) and Cr ($r = +0.955$, $P = 0.011$). All seven survive Holm–Bonferroni adjustment across the eight tests (adjusted $P = 0.0004$ – 0.033); Fe does not (adjusted $P = 0.25$). Replacing PL entirely with VW reduced the mature-product content of Cd by 98%, Ni by 85%, Pb by 79%, Cr by 77%, Zn by 76%, Cu by 70%, and Mn by 69%.

Table 2 Mature-product concentrations and the dependence of each element on blending ratio.

Element	T1	T2	T3	T4	T5	a	b	r	P
Zn	213.30	178.92	109.08	74.44	50.17	172.30	39.03	+0.985	0.002
Cu	211.30	136.35	117.50	84.44	62.37	139.91	52.44	+0.964	0.008
Fe	204.52	211.50	255.18	244.32	230.94	−34.26	246.42	−0.633	0.251
Mn	388.36	300.62	207.18	142.77	120.95	277.07	93.44	+0.979	0.004

Ni	41.55	33.10	25.00	14.11	6.19	35.88	6.05	+0.999	< 0.001
Cr	2.510	2.260	2.030	0.840	0.580	2.11	0.59	+0.955	0.011
Cd	3.340	2.290	1.600	0.078	0.060	3.51	−0.28	+0.974	0.005
Pb	9.850	7.210	6.680	2.220	2.050	8.24	1.48	+0.962	0.009

288 Columns T1–T5 give the day-90 mean concentration (mg kg^{-1} dry matter) for the blends defined in Table 1. The regression
 289 is ordinary least squares of that concentration on the PL mass fraction f_{PL} , $C = a \cdot f_{\text{PL}} + b$, fitted to the five treatment
 290 means: a , slope (mg kg^{-1} per unit f_{PL}); b , intercept (mg kg^{-1}); r , Pearson correlation coefficient; P , two-tailed probability,
 291 unadjusted, with the Holm–Bonferroni-adjusted values given in Sect. 3.1. Fe is the only element with a negative, non-
 292 significant slope, and the only one more concentrated in the VW endmember (Sect. 3.1).



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Fig. 1 Trace-element concentrations through the composting cycle across five poultry litter (PL): vegetable waste (VW) ratios. Error bars are ± 1 SE of the treatment mean ($n = 3$), derived from the analysis-of-variance error mean square. Panels (f)–(h) are shown without error bars because no error term could be validated for those elements (Sect. 2.4). Fe is labeled separately: it falls in the low-enrichment class but is excluded from the conservative reference set because it tracks mineral input (Sect. 3.1).

The linearity is itself informative. It indicates that, at the level of pseudo-total content, no strong non-additive interaction occurs between the two feedstocks: the mature product behaves as a simple mixture of its endmembers. Operationally, this means that final metal load is predictable from feedstock composition alone, so an operator who knows the metal content of an incoming PL batch can compute a permissible inclusion rate without running composting trials.

Fe was the sole exception, and the exception is diagnostic. It was the only element more concentrated in the VW endmember (230.9 mg kg⁻¹) than in pure PL (204.5 mg kg⁻¹), and the only element whose regression on PL fraction was negative and non-significant ($r = -0.633$, $P = 0.251$). VW carries adhering soil and street dust, in which Fe exceeds every other trace metal by two to three orders of magnitude. Its inversion relative to all other elements is consistent with that origin and establishes Fe as an internal tracer of mineral input to the piles, a property exploited in Sect. 3.5. For the same reason, Fe is excluded from the conservative reference set used to constrain λ .

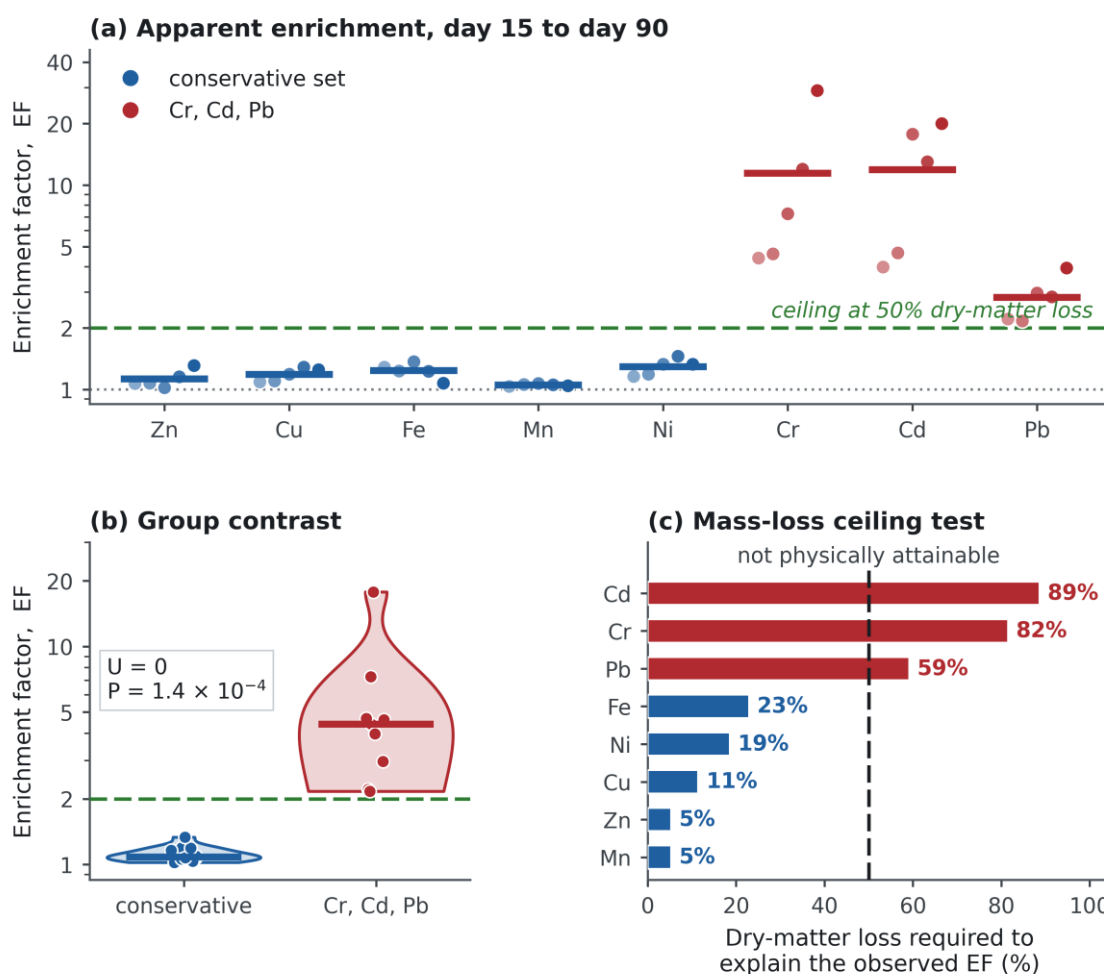
3.2 Enrichment factors separate the elements into two classes

Apparent enrichment over the composting cycle, $EF = C_{90d}/C_{15d}$, partitioned the elements into two sharply separated groups (Fig. 2a, Table 3).

Table 3 Apparent enrichment of each element over the composting cycle.

Element	Class	T1	T2	T3	T4	T5	Mean (T1–T3)	Minimum θ_0 (%) ^a
Zn	Conservative	1.07	1.07	1.02	1.16	1.31	1.06	0
Cu	Conservative	1.09	1.10	1.19	1.29	1.25	1.13	4
Fe	Mineral tracer	1.29	1.23	1.37	1.23	1.08	1.30	16
Mn	Conservative	1.04	1.06	1.07	1.06	1.04	1.06	0
Ni	Conservative	1.16	1.19	1.33	1.45	1.33	1.23	11
Cr	Non-conservative	4.40	4.61	7.25	12.00	29.00	5.42	80
Cd	Non-conservative	3.98	4.67	17.78	13.00	20.00	8.81	88
Pb	Non-conservative	2.21	2.17	2.97	2.85	3.94	2.45	56

$EF = C_{90d}/C_{15d}$, the ratio of the day-90 to the day-15 mean, given for each blend T1–T5. Class assigns the element to the behavioral group used throughout: conservative, mineral tracer (Fe alone, Sect. 3.1) or non-conservative. Mean (T1–T3) averages the three litter-rich blends, in which every concentration lies well above the detection limit. ^a Minimum fraction of the metal inventory unrecovered at the first sampling, $\theta_0 \geq 1 - 1/\lambda$, Eq. (8), evaluated on the T1–T3 mean liberation factor under the tracer-based mass-loss scenario.



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Fig. 2 The conservation test. (a) Apparent enrichment factor by element; horizontal bars are element means and points are individual treatments. The dashed line marks the ceiling of EF = 2.0 set by 50% dry-matter loss, the maximum attainable by matrix shrinkage alone. (b) Group contrast restricted to treatments T1–T3, where all concentrations lie well above detection limits. (c) Dry-matter loss that would be required to explain each element’s observed enrichment by shrinkage alone, $L = 1 - 1/EF$, evaluated at the T1–T3 mean; values beyond the dashed line at 50% are not attainable in a composting pile.

Zn, Cu, Fe, Mn and Ni enriched by factors of 1.02–1.45, with a pooled mean of 1.18. Mn was near-static across every treatment (1.04–1.07), Zn changed by 2–31%, and Ni showed the largest change within this group (1.16–1.45). These magnitudes correspond to dry-matter losses of 2–31%, entirely consistent with expectation for a turned pile over this interval.

Cr, Cd and Pb enriched by factors of 2.17–29.0, with a pooled mean of 8.7. In treatment T1, which carries the highest absolute concentrations and is therefore least susceptible to detection-limit artifacts, Cd rose from 0.84 to 3.34 mg kg⁻¹ (3.98×), Cr from 0.57 to 2.51 mg kg⁻¹ (4.40×) and Pb from 4.45 to 9.85 mg kg⁻¹ (2.21×).

Restricting the comparison to T1–T3, where every concentration lies well above analytical detection limits, the conservative set averaged EF = 1.12 (range 1.02–1.33, n = 12, Fe excluded) against 5.56 for Cr, Cd and Pb (range 2.17–17.78, n = 9). The distributions do not overlap at any point (Mann–Whitney U = 0, P = 1.4×10^{-4} ; Fig. 2b). Because each element contributes one value to each treatment, those 21 units are not mutually independent, and the probability attaching to them is correspondingly optimistic. Repeating the contrast on element means, which are independent, again returns complete separation (U = 0) at the smallest value the number of elements admits (exact two-sided P = 0.057 for four elements against three). No test on seven elements can return less, so the argument rests on the completeness of the separation and on the size of the effect rather than on the probability alone. The very large enrichment factors recorded in T4 and T5 (to 29×) arise from ratios of near-detection-limit values and are not relied upon; the separation is fully established within T1–T3 alone.

3.3 Matrix mass loss cannot account for the second class

The mass-loss ceiling test is shown in Fig. 2c. For a conservative element, enrichment is bounded by $1/(1 - L)$. A pile losing 30% of its dry matter can produce at most 1.43-fold enrichment; one losing 50%, an upper bound for turned windrow composting, at most 2.00-fold. Every one of the 12 conservative-set values in T1–T3 falls below the 2.00 ceiling. Every one of the nine Cr, Cd and Pb values exceeds it.

The magnitude of the shortfall is decisive rather than marginal. To generate the observed mean enrichment of 8.7 by mass loss alone would require $L = 88.5\%$, which is not physically attainable in a composting pile and is, in any case, contradicted by the conservative elements measured in the same digests from the same piles, which imply $L \approx 15\%$. No single value of L can simultaneously satisfy both groups. The two classes therefore cannot both be conservative.

3.4 The liberation factor is robust to the mass-loss assumption

Partitioning each trajectory into matrix-loss and liberation components with Eq. (7) makes this conclusion quantitative and tests its dependence on the unmeasured parameter λ (Fig. 3, Table 4).

Table 4 Liberation factor under three assumptions about dry-matter loss.

Element	Λ , tracer-based	Λ , 30% DM loss	Λ , 50% DM loss
Zn	0.97	0.74	0.53
Cu	1.04	0.79	0.56
Fe	1.19	0.91	0.65
Mn	0.97	0.74	0.53
Ni	1.13	0.86	0.61
Cr	4.99	3.80	2.71
Cd	8.10	6.17	4.40
Pb	2.25	1.71	1.22
Conservative set (mean)^a	1.03	0.78	0.56
Cr, Cd, Pb (mean)	5.11	3.89	2.78
P (Mann–Whitney)	1.4×10^{-4}	1.4×10^{-4}	1.4×10^{-4}

$\Lambda = [C(t)/C(t_0)] e^{-\lambda \Delta t}$, Eq. (7), is the part of the concentration change that matrix loss cannot account for; $\Lambda = 1$ denotes fully conservative behavior. Entries are means over the three litter-rich blends T1–T3. The three scenarios fix λ so that dry-matter loss over the 75-day window is 8.1% (estimated from Zn and Mn as conservative tracers), 30% and 50% respectively. P is the two-tailed Mann–Whitney probability for the contrast between the two groups. ^a The conservative set comprises Zn, Cu, Mn and Ni; Fe is excluded as a tracer of mineral input (Sect. 3.1). $\Lambda < 1$ is physically inadmissible for a fully recovered element and indicates that the corresponding scenario overstates dry-matter loss.

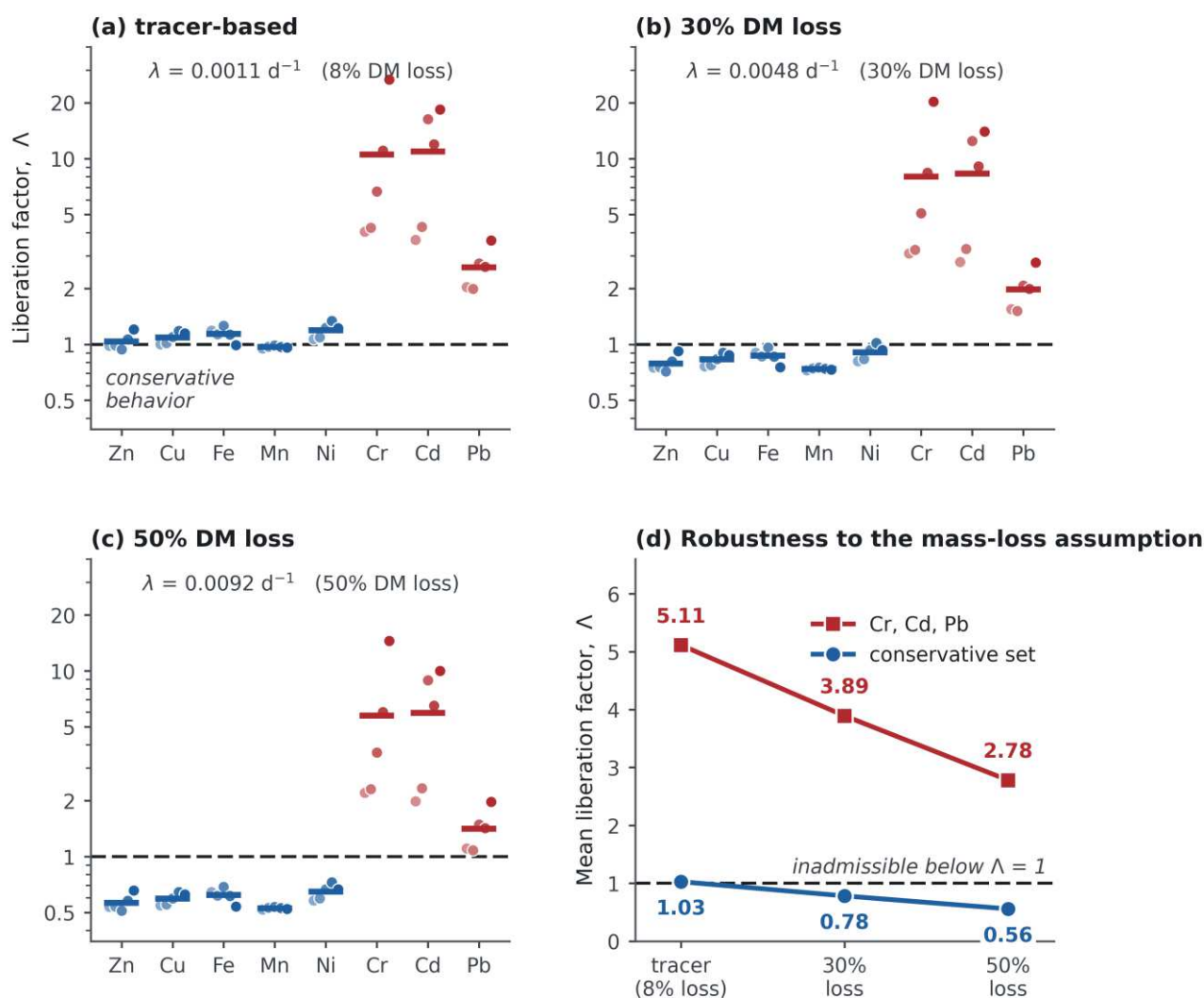


Fig. 3 Liberation factor Λ under three dry-matter-loss scenarios. (a) Tracer-based, (b) 30% loss, (c) 50% loss; points are individual treatments and horizontal bars are element means. Values below the dashed line at $\Lambda = 1$ are physically inadmissible for a fully recovered element. (d) Robustness of the group separation: the conservative set converges on unity only under the tracer-based scenario, while Cr, Cd and Pb remain well above unity under every scenario.

Under the tracer-based scenario S1, in which Zn and Mn are assumed conservative and yield $\lambda = 0.00112 \text{ d}^{-1}$ (8.1% dry-matter loss over the window), the conservative set returned a mean liberation factor of $\Lambda = 1.03$, indistinguishable from unity, as required for internal consistency, while Cr, Cd and Pb returned $\Lambda = 5.11$ ($U = 0$, $P = 1.4 \times 10^{-4}$). Element-wise values were Zn 0.97, Mn 0.97, Cu 1.04, Ni 1.13 and Fe 1.19 against Cr 4.99, Cd 8.10 and Pb 2.25.

Forcing λ upward progressively suppresses Λ for every element, but does not close the gap. At 30% dry-matter loss, the conservative set falls to $\Lambda = 0.78$ and the toxic set to 3.89; at 50% loss, to 0.56 and 2.78 respectively (Fig. 3d). The separation remains significant at identical probability throughout, because the two groups never overlap.

Critically, the conservative elements bound λ from above. A liberation factor below unity is physically impossible for an element already fully recovered at the first sampling, since it would require the digestion to recover *less* metal from a more humified matrix. That the conservative set drops to $\Lambda = 0.78$ at 30% loss and 0.56 at 50% loss indicates that both scenarios overstate the true dry-matter loss for these piles, and that the tracer-based estimate is the physically admissible one. Even under the inadmissible 50% scenario, however, Cr, Cd and Pb still require $\Lambda = 2.78$. The inference that these elements are non-conservative is therefore independent of any assumption about mass loss.

Applying Eq. (8), the minimum fraction of the inventory unrecovered at the first sampling was 80% for Cr, 88% for Cd and 56% for Pb, against 4–16% for Cu, Ni and Fe and indistinguishable from zero for Zn and Mn.

3.5 Fe excludes mineral ingress as an alternative explanation

Because the pits were unlined, incorporation of soil during turning is an *a priori* plausible route by which metal mass could enter a pile and violate the conservation assumption. Fe bounds it.

The Fe increase in T1 (+45.8 mg kg⁻¹) is fully explained by incorporation of 0.13% w/w mineral matter, taking a world mean soil Fe content of 35,000 mg kg⁻¹. That same 0.13% addition contributes +0.078 mg kg⁻¹ Cr, +0.030 mg kg⁻¹ Pb and -0.0006 mg kg⁻¹ Cd, that is, 4.0%, 0.6% and -0.02% of the increases actually observed.

For Cd the argument is stronger still. World mean soil Cd (0.41 mg kg⁻¹) lies *below* the initial compost concentration (0.84 mg kg⁻¹), so mineral ingress would dilute Cd rather than raise it; no finite incorporated fraction can generate the observed increase. Solving independently for Pb would require 24% mineral incorporation, which would have raised Fe by some 8300 mg kg⁻¹ against the 46 mg kg⁻¹ observed, an inconsistency of two orders of magnitude. Mineral ingress is therefore excluded.

With matrix loss bounded by the conservative elements and external addition bounded by Fe, the remaining explanation is that the recovered fraction $f(t)$ increased. The measurement changed; the inventory did not.

3.6 Liberation follows first-order kinetics on a composting timescale

Liberation trajectories and their fitted kinetics are shown in Fig. 4 and Table 5. Equation (10) described the Cr, Cd and Pb data well, with R^2 of 0.934–0.964, 0.950–0.996 and 0.894–0.943, respectively. The pooled liberation rate constant was $k = 0.0143 \pm 0.0072$ d⁻¹, corresponding to a half-time of 49 days, comfortably within a normal composting cycle, which is precisely why the effect is large enough to matter operationally.

Table 5 First-order kinetics of liberation, and the comparison against a conservative null.

Element	Treatment	Λ_∞	k (d ⁻¹)	$t_{1/2}$ (d)	R^2	ΔAIC_c^a	$w(\text{lib.})$
Cr	T1	4.42	0.0149	46	0.953	-10.6	0.995
	T2	9.93	0.0041	169	0.934	-7.1	0.973
	T3	15.08	0.0048	144	0.964	-11.3	0.996
Cd	T1	4.07	0.0138	50	0.950	-10.1	0.994
	T2	4.34	0.0159	44	0.996	-26.4	1.000
	T3	17.35	0.0187	37	0.976	-15.5	1.000
Pb	T1	1.70	0.0285	24	0.943	-10.5	0.995
	T2	1.90	0.0144	48	0.894	-5.1	0.927
	T3	2.91	0.0135	51	0.903	-5.6	0.943
Cu	T1–T3	1.00	—	—	n.d. ^b	+15.0	0.001
Ni	T1–T3	1.00	—	—	n.d. ^b	+15.0	0.001

Fitted to $\Lambda(t) = \Lambda_\infty - (\Lambda_\infty - 1) e^{-k\Delta t}$, Eq. (10), under the 30% dry-matter-loss scenario, separately for each element $\times$ treatment series: Λ_∞ , ultimate liberation ratio; k , liberation rate constant; $t_{1/2} = \ln 2/k$, liberation half-time; R^2 , proportion of the variance in $\Lambda(t)$ accounted for by the fit; $w(\text{lib.})$, Akaike weight of the liberation model. Cu and Ni are fitted as null controls. ^a Negative ΔAIC_c favors the liberation model over the null $\Lambda = 1$; values below -4 denote strong support. ^b n.d., not determined; the fit returned $\Lambda_\infty = 1.00$, so both models describe the data equally well, and ΔAIC_c reduces to the penalty for the extra parameters.

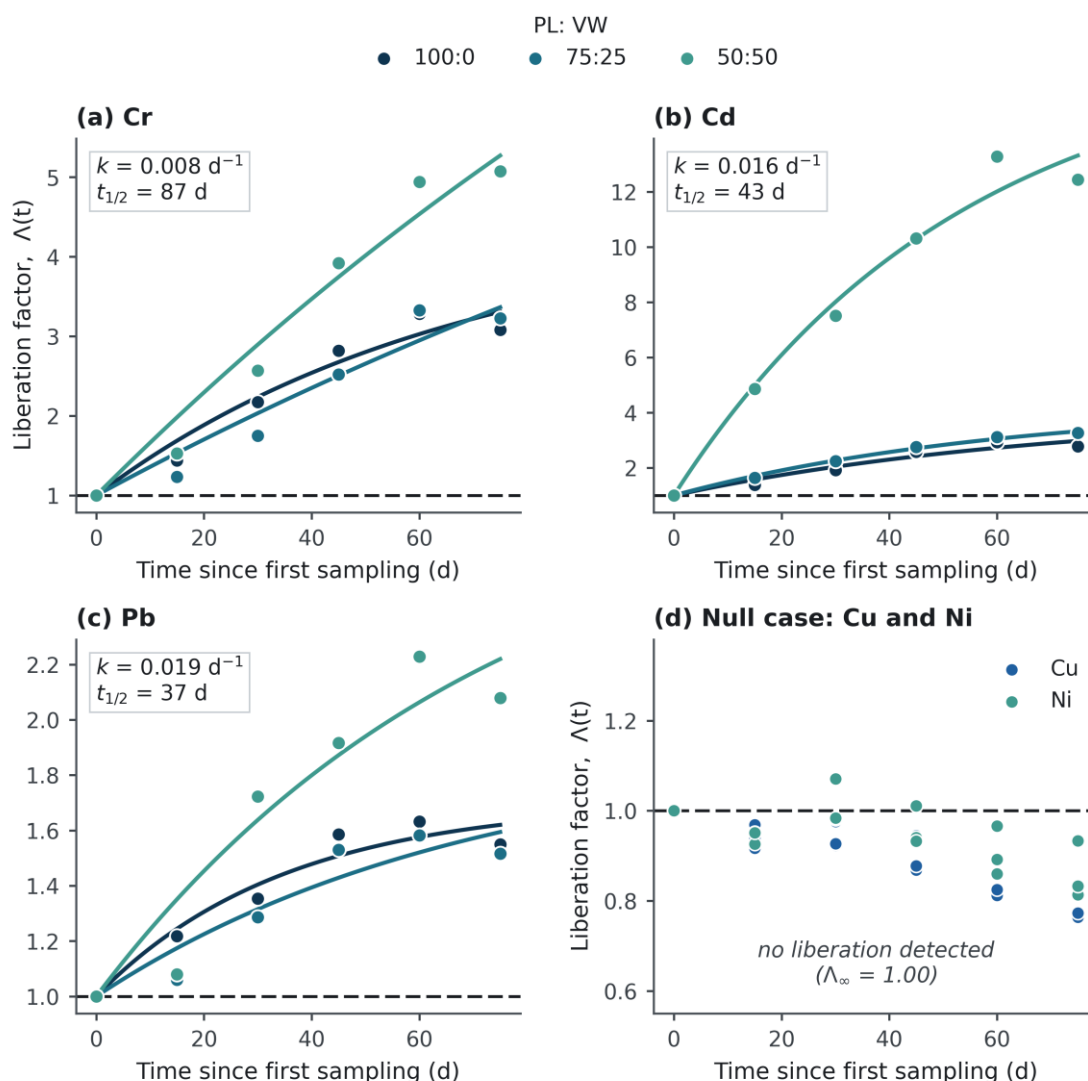


Fig. 4 Kinetics of liberation. (a)–(c) $\Lambda(t)$ trajectories for Cr, Cd and Pb in treatments T1–T3 with first-order fits to Eq. (10); insets give the mean rate constant and half-time. (d) Null controls: Cu and Ni show no liberation signal ($\Lambda_{\infty} = 1.00$).

The three elements differed systematically in rate. Pb liberated fastest ($k = 0.019 \text{ d}^{-1}$, $t_{1/2} = 37 \text{ d}$) but to the smallest extent ($\Lambda_{\infty} = 1.70\text{--}2.91$); Cd was intermediate in rate ($k = 0.016 \text{ d}^{-1}$, $t_{1/2} = 43 \text{ d}$) and large in extent ($\Lambda_{\infty} = 4.07\text{--}17.35$); Cr was slowest ($k = 0.008 \text{ d}^{-1}$, $t_{1/2} = 87 \text{ d}$) and had not approached its asymptote by the end of the cycle. The ordering is consistent with progressively more refractory host phases: Pb associated with readily degraded organic and carbonate fractions, Cd with organic and sulfide-like associations, and Cr with the most recalcitrant residual pool.

Cu and Ni, fitted as null controls, returned $\Lambda_{\infty} = 1.00$ with no detectable liberation (Fig. 4d), confirming that the model does not manufacture a liberation signal where none exists.

3.7 Model comparison favors liberation in every toxic series

Because the series are short and lack a validated replicate error term for the three metals of interest, the comparison between the liberation model and the conservative null was also framed in information-theoretic terms (Fig. 5c, Table 5). The result is unambiguous. For Cr, Cd, and Pb, the liberation model was favored in **all nine** element $\times$ treatment series, with a mean ΔAIC_c of -11.4 and Akaike weights of $0.93\text{--}1.00$; the strongest support was for Cd in T2 ($\Delta\text{AIC}_c = -26.4$). For the conservative elements, the null was favored in **all twelve** series, with a mean ΔAIC_c of $+15.0$. The positive value is itself diagnostic: when the fitted liberation model collapses onto the null ($\Lambda_{\infty} = 1.00$), the two models describe the data equally well, and the difference reduces to the penalty for the two additional parameters, which is exactly what is observed.

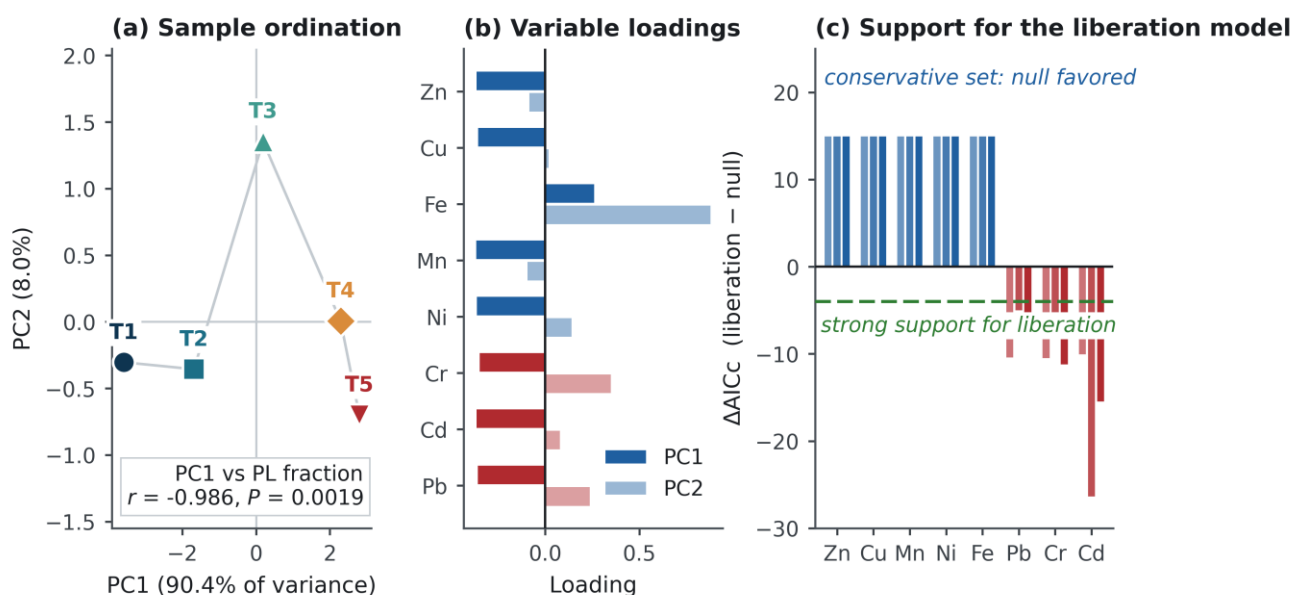


Fig. 5 Ordination and model support. (a) Sample scores on the first two principal components of the standardized 90-day composition; the five treatments order monotonically along PC1, which tracks the PL fraction. (b) Variable loadings: every element except Fe loads on PC1 with almost identical weight, whereas Fe loads oppositely and dominates PC2. (c) Difference in small-sample corrected Akaike information criterion between the liberation model of Eq. (10) and the conservative null $\Lambda = 1$, for each element and treatment. Negative values favor liberation, and the dashed line at -4 marks strong support; the constant positive value for the conservative elements arises because the fitted liberation model collapses onto the null, leaving only the penalty for the additional parameters.

The bootstrap intervals reinforce the separation. Under the tracer-based scenario, the conservative set returned $\Lambda = 1.03$ with a 95% interval of $[0.99, 1.07]$ that contains unity, as internal consistency requires, against $\Lambda = 5.11$ $[3.05, 8.23]$ for Cr, Cd and Pb. The intervals are disjoint, and remain so under the 30% scenario ($[0.75, 0.82]$ against $[2.31, 6.26]$) and the 50% scenario ($[0.54, 0.58]$ against $[1.65, 4.46]$).

3.8 Ordination confirms a single compositional gradient

Spearman rank correlations among the eight elements in the mature products were $+1.00$ for every pair not involving Fe, and -0.60 for all seven pairs that did. The perfect rank concordance follows from the fact that each element except Fe is monotone in the blending ratio across five treatments, so the coefficient is descriptive rather than informative; it does, however, isolate Fe as the only element that does not follow the litter gradient.

Principal component analysis makes the same point quantitatively (Fig. 5a, b). The first component accounted for 90.4% of the variance and the second for 8.0%, together more than 98%. All elements except Fe loaded on PC1 with almost identical weight (-0.35 to -0.37), while Fe loaded positively ($+0.26$) and dominated PC2 ($+0.88$). Sample scores on PC1 tracked the PL fraction almost perfectly ($r = -0.986$, $P = 0.0019$), ordering the five treatments monotonically from T1 to T5. The composition of the mature product is therefore governed by a single mixing gradient, with Fe the sole independent dimension, consistent with its origin as adhering mineral matter rather than a feed-derived constituent (Sect. 3.1).

3.9 The compliance verdict inverts within a single composting cycle

Mature-product concentrations against statutory limits are given in Table 6. **Cd was the sole binding constraint under Regulation (EU) 2019/1009.** Ni reached at most 83% of its limit (41.6 against 50 mg kg⁻¹), Cu 70% (211.3 against 300), Zn 27% (213.3 against 800), and Pb 8% (9.9 against 120). Cd exceeded its 1.5 mg kg⁻¹ limit in all three PL-rich treatments, reaching 223%, 153%, and 107% of the limit in T1, T2, and T3, respectively. All treatments complied comfortably with the more permissive US EPA limits, the highest value reaching 14% of the Cu ceiling.

Table 6 Mature-product concentrations against statutory contaminant limits.

Element	EU 2019/1009	US EPA 503	100:0	75:25	50:50	25:75	0:100	Highest as % of EU limit
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Cd	1.5	39	3.340 ^a	2.290 ^a	1.600 ^a	0.078	0.060	223
Ni	50.0	420	41.55	33.10	25.00	14.11	6.19	83
Cu	300.0	1,500	211.30	136.35	117.50	84.44	62.37	70
Zn	800.0	2,800	213.30	178.92	109.08	74.44	50.17	27
Pb	120.0	300	9.850	7.210	6.680	2.220	2.050	8

455 Concentrations (mg kg⁻¹ dry matter) of the day-90 product; the five column headings give the PL: VW blend as in Table 1.
456 The Cd, Ni and Pb ceilings are those of Annex II, Component Material Category 3 (compost) of Regulation (EU)
457 2019/1009; the Cu and Zn ceilings are those of Annex I, Product Function Category 3(A) (organic soil improver), which
458 governs the finished product. Where both annexes set a Cd limit, the stricter Component Material Category 3 value of 1.5
459 mg kg⁻¹ is binding. US EPA 503 is the “pollutant concentration” limit of 40 CFR 503.13. The final column gives the
460 highest of the five blends as a percentage of the EU limit. Cr was determined as total Cr, whereas the EU limit applies to
461 Cr(VI), so Cr is not assessable and is omitted. ^a Exceeds the EU limit.

462 The liberation result has a direct and unwelcome consequence for monitoring. Because measured Cd in T1 rose from 0.84
463 mg kg⁻¹ at the first sampling to 3.34 mg kg⁻¹ at the last, the compliance verdict for a single unchanged pile inverts during
464 the cycle: sampled at 15 or 30 days it reports as compliant (0.84 and 1.25 mg kg⁻¹), and from 45 days onward as non-
465 compliant (1.86 rising to 3.34 mg kg⁻¹). The same inversion occurs in T2, compliant to day 45 and non-compliant from
466 day 60, and in T3, compliant to day 60 and marginally non-compliant thereafter. Sampling time is thus a determinant of
467 the regulatory outcome, in the absence of any change in the metal content of the material.

468 The Monte-Carlo model (Fig. 6a) converts this into a decision rule with explicit residual risk. Exceedance probability rises
469 steeply between 30% and 60% PL. Exceedance risk reaches 5% at a PL share of 37%, 10% at 40%, 25% at 45%, and 50%
470 at 51%; these are the inclusion rates at which the modeled probability equals each tolerance, obtained by interpolation on
471 the risk curve, so a share at or below the quoted value is the one that meets the corresponding criterion. A conventional
472 50:50 blend therefore carries approximately even odds of breaching the limit, which is unlikely to be an acceptable
473 operating point for a product entering the food-production chain.

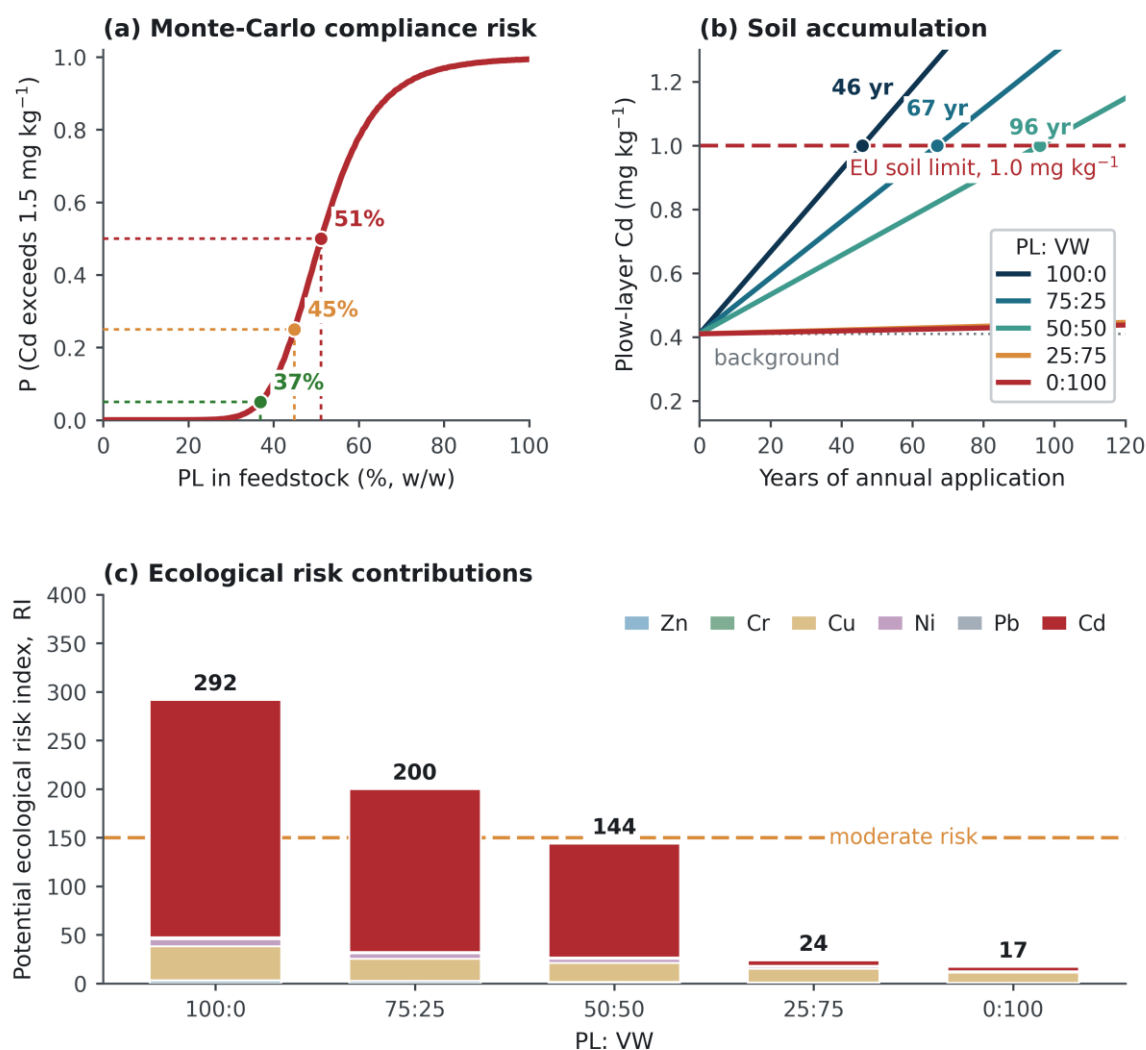


Fig. 6 Risk models. (a) Monte-Carlo exceedance probability for the EU Cd limit as a function of PL share, propagating regression and analytical uncertainty (2×10^5 realizations per point); markers indicate the 5%, 25% and 50% risk thresholds. (b) Plow-layer Cd accumulation under continuous annual application at $10 \text{ Mg ha}^{-1} \text{ yr}^{-1}$. (c) Potential ecological risk index partitioned by element; Cd dominates despite contributing a negligible share of the trace-metal mass.

3.10 Cd dominates ecological risk and long-term soil loading

Geochemical indices for the mature products are given in Table 7 and Fig. 6c. Contamination factors relative to world mean soil were dominated by Cd ($\text{CF} = 8.15$ in T1) and Cu ($\text{CF} = 7.04$), with Zn intermediate ($\text{CF} = 3.05$), Ni only marginally above unity ($\text{CF} = 1.43$) and Cr, Pb, and Mn all below it (that is, below typical soil concentrations). The pollution load index fell from 1.25 in T1, indicating a net enrichment relative to soil, to 0.18 in T5. Geoaccumulation indices, Eq. (13), place the same result on Müller's classification. Only Cd, Cu and Zn exceeded zero in any treatment. Cd reached $I_{\text{geo}} = 2.44$ in T1, the only value in the moderately to heavily polluted class, falling to 1.90 in T2 and 1.38 in T3, both moderately polluted, and to -2.98 and -3.36 in T4 and T5, which are unpolluted. Cu behaved similarly but with a much shallower gradient, from 2.23 in T1 to 0.47 in T5, so it was the only element still above zero in the pure-VW product. Cr, Mn, Ni and Pb were below zero throughout, Cr by more than five doubling units.

Table 7 Geochemical indices and the soil-loading horizon for the mature composts.

Treatment	CF_{Zn}	CF_{Cu}	CF_{Ni}	CF_{Cd}	PLI	RI	Cd share of RI (%)	Years to soil limit ^a
T1 (100:0)	3.05	7.04	1.43	8.15	1.25	292	84	46
T2 (75:25)	2.56	4.54	1.14	5.59	0.95	200	84	67
T3 (50:50)	1.56	3.92	0.86	3.90	0.75	144	81	96

T4 (25:75)	1.06	2.81	0.49	0.19	0.26	24	24	1,967
T5 (0:100)	0.72	2.08	0.21	0.15	0.18	17	26	2,557

CF, contamination factor, the day-90 concentration divided by the world mean soil concentration (Kabata-Pendias, 2011); PLI, pollution load index, the geometric mean of CF; RI, potential ecological risk index, the toxic-response-weighted sum of CF (Hakanson, 1980); Cd share of RI, the percentage of RI contributed by Cd alone. PLI and RI are computed over the six weighted elements (Zn, Cr, Cu, Ni, Pb, Cd). Contamination factors for Cr (≤ 0.04), Pb (≤ 0.37) and Mn (≤ 0.79) lie below unity in every treatment and are omitted for space; Mn and Fe carry no toxic-response weighting and enter neither index. Risk classes: $RI < 150$ low, 150–300 moderate. ^a Years of continuous application at 10 Mg ha⁻¹ yr⁻¹ before plow-layer Cd reaches 1.0 mg kg⁻¹, Eq. (16).

The potential ecological risk index decreased monotonically with PL share, from 292 (moderate risk) in T1 through 200 (moderate) in T2 to 144, 24 and 17 (all low) in T3, T4 and T5. **Cd alone contributed 81–84% of the total index in the three PL-rich treatments**, despite being present at less than one-sixtieth the concentration of Zn, a direct consequence of its toxic-response weighting. Ecological risk in this system is effectively a Cd problem.

The soil-accumulation model (Fig. 6b, Table 7) places this in a management timeframe. At an application rate of 10 Mg ha⁻¹ yr⁻¹, continuous use of the pure-PL compost would raise plow-layer Cd from a background of 0.41 mg kg⁻¹ to the 1.0 mg kg⁻¹ limit of Directive 86/278/EEC in 46 years; the 75:25 and 50:50 blends extend this to 67 and 96 years. The 25:75 blend extends it to roughly 2000 years, and the pure-VW compost to 2600 years. Doubling the application rate halves each interval. The distinction between the PL-rich and VW-rich blends is therefore not a marginal difference in loading rate but a difference between an agronomically relevant horizon of a few decades and one of geological irrelevance.

3.11 The lowest-metal blends are the most saline and the most acidic

Final pH declined monotonically with VW share, from 7.35 in pure PL to 6.25 in pure VW, while electrical conductivity rose from 5.26 to 11.50 dS m⁻¹ (Table 1). Every element except Fe correlated positively with final pH ($r = +0.89$ to $+0.98$) and negatively with final electrical conductivity ($r = -0.90$ to -1.00). These correlations arise from the shared dependence of all three variables on blending ratio and are not evidence of causation. They do, however, describe a practically important tension: the blends with the lowest total metal loads are also the most acidic and by far the most saline, conditions that favor metal solubility and, at 10.8–11.5 dS m⁻¹, are high enough to damage sensitive seedlings without prior dilution.

4 Discussion

The models in this paper are instruments, not findings. What survives them is a single physical statement: the metal inventory of these piles did not change while the fraction of it a standard digestion could reach did. Four things follow, and a reader can carry each away independently of any model: a test they can run on their own existing data, a different reading of the sequential-extraction literature, a defect in how compost compliance is sampled and measured, and a blending rule for this feedstock pair expressed as a risk rather than a point estimate. The sections below take each in turn.

4.1 The liberation signal records rising analytical recovery

The partition analysis places a firm constraint on interpretation. Metal mass is conserved; matrix loss is bounded from above by the conservative elements at roughly 8–15%; external mineral input is bounded by Fe at 0.13% w/w. Yet measured Cr, Cd and Pb rise 2.2- to 4.4-fold in T1, the treatment carrying the highest concentrations and therefore the least exposed to detection-limit artifacts, and require $\Lambda \gg 1$ under every mass-loss scenario including physically inadmissible ones. The inference is unavoidable: what changed over the composting cycle was the recovery of the analytical method, not the metal inventory of the pile.

The mechanism we regard as most parsimonious (Fig. 7) is a progressive increase in the efficiency with which a nitric–perchloric digestion extracts metal from a humifying substrate. Fresh PL and VW are dominated by lignocellulosic material in which trace metals are partly occluded within recalcitrant polymeric structures and within mineral inclusions carried through the feed chain. Hot nitric–perchloric acid is aggressive but does not constitute a total digestion: it leaves silicate residues substantially intact, and its recovery is demonstrably matrix- and method-dependent in composts specifically: Hseu (2004) found nitric–perchloric digestion to recover less Cd, Mn and Ni from compost than nitric acid

alone. As composting proceeds, lignocellulose is depolymerized, and the residue converts to humic substances bearing abundant carboxyl and phenolic groups that complex metals in forms readily released by acid attack. Metal that was analytically invisible at the first sampling becomes visible by the last.

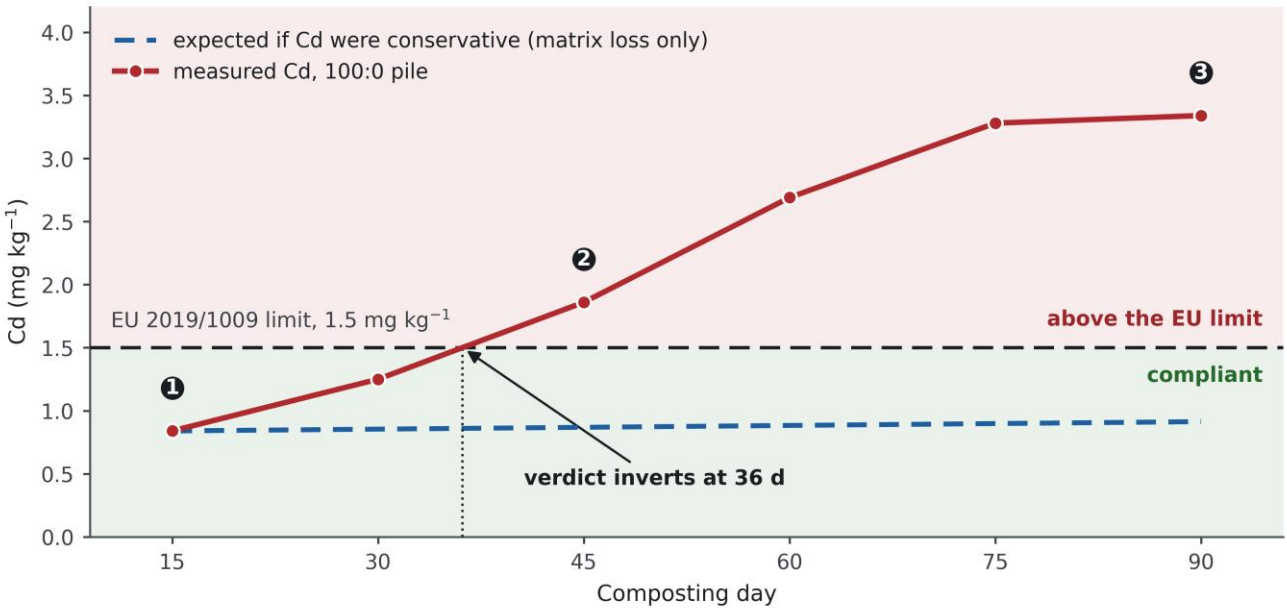
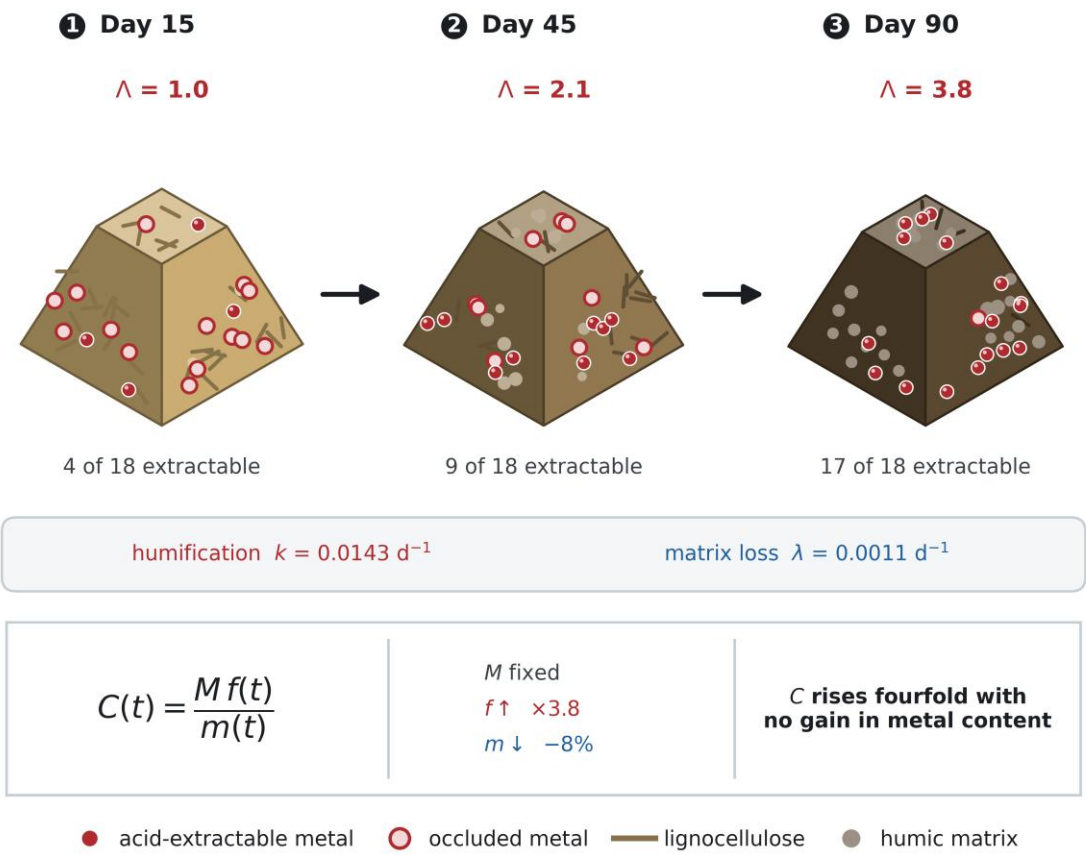


Fig. 7 Conceptual model of the composting cycle, drawn in isometric projection. Upper panel: the same pile at three points in the cycle. Each heap carries an identical, fixed number of metal units, so the inventory M is conserved; the volume shown shrinks by the measured dry-matter loss. As the tan lignocellulosic matrix is depolymerized to dark humic material (rate k), metal that was occluded and therefore invisible to a pseudo-total digestion (open symbols) passes into acid-

extractable association with humic functional groups (filled symbols), while matrix mass is lost at the much slower rate λ . The particle counts are illustrative; the liberation factors Λ are those measured for Cd in T1. Lower panel: the same sequence in the data. Measured Cd rises fourfold while the trajectory expected of a conservative element under matrix loss alone (dashed) stays almost flat, and the compliance verdict for one unchanged pile crosses the EU limit part-way through the cycle.

This mechanism predicts precisely the pattern observed, and the prediction is non-trivial. The elements that behaved conservatively are those entering the system predominantly as soluble ionic species and weakly bound surface complexes (Zn and Cu supplied deliberately as feed additives, Mn and Fe as ionic constituents), and therefore fully recoverable from the outset. The elements showing large liberation are trace contaminants entering as impurities within phosphate supplements and mineral premixes (Nicholson et al., 1999), which is exactly the pathway most likely to deliver metal in refractory host phases. The apparent liberation ordering (Pb fastest but smallest, Cd intermediate, Cr slowest and largest) tracks the expected stability of those host phases.

Our findings are consistent with, and offer a reinterpretation of, the substantial sequential-extraction literature on composting. Numerous studies report redistribution of metals from residual to organically bound and exchangeable fractions during maturation of sludges and manures (Amir et al., 2005; Liu et al., 2007; He et al., 2009; Zheng et al., 2007). That literature has generally framed such redistribution as a change in *speciation*, with implications for bioavailability. The present analysis suggests a complementary and largely overlooked corollary: if the residual fraction is the one that a pseudo-total digestion systematically under-recovers, then the same redistribution must also inflate the apparent *total* content. Speciation change and apparent total-content change are two readings of one process.

We present this as the best-supported explanation rather than a demonstrated one, and the distinction matters. Two alternatives cannot be eliminated from these data alone. The first is systematic analytical drift across the sampling campaign; this would, however, have to have affected Cr, Cd and Pb while sparing Zn, Cu, Fe, Mn and Ni measured in the same digests on the same instrument, which is difficult to construct. The second is a genuine chemical transformation that changes extractability without changing speciation in the operational sense. Distinguishing these requires a purpose-designed experiment, discussed in Sect. 4.8.

4.2 Analytical uncertainty cannot generate the liberation signal

The absence of a validated replicate error term for Cr, Cd and Pb invites three specific objections. Each can be answered quantitatively rather than by assertion.

Could analytical scatter bias Λ upward? It could, because Λ is a ratio and a noisy denominator inflates the expectation of a ratio. The size of that bias is calculable. Modeling the analytical error as lognormal, which is the appropriate form for a multiplicative error and avoids the artifacts a normal model produces in the tail, and taking the largest CV reported for Cd anywhere in this dataset, 20.8%, the expected value of $C(90\text{ d})/C(15\text{ d})$ for an element whose true concentration did not change is 1.043 rather than unity. Analytical scatter therefore inflates Λ by 4.3%, which is 1.1% of the gap between the conservative set at 1.03 and Cr, Cd and Pb at 5.11. The bias is real; it acts in the direction the objection supposes, and it is two orders of magnitude too small to matter.

Could scatter alone produce the observed Λ ? Under the same error model, with a true liberation factor of unity, the probability that a single series returns an apparent Λ of 5.11 or more is 1.9×10^{-9} . Put the other way round, the analytical CV would have to reach 85%, four times the largest value reported anywhere in this dataset, before a single series had even a one-in-twenty chance of producing that value by measurement error alone. For the mean of nine series, the quantity actually reported, the probability remains numerically zero at a CV of 50%, and the error would have to exceed 100%, that is, be larger than the signal it is measuring, before the group mean reached 5.11 with even a one-in-a-hundred chance.

Could variability in the digestion itself mimic liberation? Not in this design, because every element is determined in the same digest. A batch in which the digestion ran hot or long recovers more of everything in that solution, so its effect is common to all eight elements and cancels in the between-element contrast on which the argument rests. For digestion variability to produce the observed result, it would have to raise the recovery of Cr, Cd and Pb while leaving Zn, Cu, Fe, Mn and Ni unchanged in the same solution. That is not variability but a systematic, element-selective change in recovery, which is precisely the mechanism proposed in Sect. 4.1.

589 A fourth line of evidence is independent of any error model. Random error produces scatter, not ordered ascent, yet all
590 nine Cr, Cd and Pb series rise strictly monotonically across all six sampling occasions, against six of the twelve
591 conservative series (Fisher exact $P = 0.017$), and the information criterion prefers a smooth saturating curve to a constant
592 in all nine. What the missing error term limits is the precision that can be attached to any single treatment mean. It does not
593 reach a conclusion built on the sign, the magnitude, and the shape of a contrast measured between elements within the
594 same digests.

595 **4.3 Compliance monitoring must be tied to product maturity**

596 If pseudo-total recovery rises with maturity, then compliance testing performed on immature compost systematically
597 under-reports the toxic trace metals. The magnitude here is not marginal: a sample drawn at 15 days understates the final
598 measured Cd content of the same pile by a factor of four, and inverts the compliance verdict.

599 Three consequences follow for regulatory practice.

600 First, **any monitoring regime that permits sampling at an unspecified point in the process is exploitable**, whether or
601 not anyone intends to exploit it. A producer sampling early obtains a systematically more favorable result at no cost and
602 with no deception. Compliance sampling should therefore be tied explicitly to the mature product, and maturity should be
603 established by an independent criterion such as germination index, respirometric activity, or a defined humification ratio,
604 rather than by elapsed time, since the rate of humification varies with feedstock, aeration and climate.

605 Second, **regulatory digestion protocols should specify a total or near-total method**, incorporating hydrofluoric acid or
606 an equivalent silicate-dissolving step, rather than a pseudo-total attack. A matrix-dependent method makes the reported
607 value a function of maturity as well as of content, which is precisely the property a compliance measurement must not
608 have.

609 Third, **comparisons between published studies that sampled at different maturities are not straightforward**, and
610 meta-analyses of compost metal content should treat sampling maturity as a covariate rather than a nuisance. Some of the
611 heterogeneity in the literature on metal behavior during composting, where reports of increases, decreases, and no change
612 coexist, may reflect differences in when the pile was sampled and how aggressively it was digested, rather than genuine
613 differences between systems.

614 **4.4 Poultry litter should not exceed about 37% of the feedstock**

615 The dose–response and Monte-Carlo results give a direct operational answer for this feedstock pair, and one expressed in
616 the language of risk rather than of point estimates. Cd governs; every other regulated element remains comfortably within
617 limits at all blends. A 25:75 PL: VW blend was compliant by a wide margin (0.078 against 1.5 mg kg^{-1}) and carries
618 negligible exceedance probability. A 50:50 blend sits near the median-risk point, with roughly even odds of breaching the
619 limit once analytical uncertainty is propagated. Operators seeking a defensible margin should target no more than about
620 37% PL, the share at which the exceedance risk reaches 5%, and below it for a wider margin.

621 Two considerations qualify this. The first is agronomic. VW-rich mixtures are markedly more saline; at $10.8\text{--}11.5 \text{ dS m}^{-1}$,
622 the 25:75 and pure-VW products would require dilution, blending or leaching before use on salt-sensitive crops. They are
623 also more acidic, which at equal total content favors metal solubility. Dilution reduces the total burden while shifting the
624 residual burden toward a more mobile chemical environment, and the optimum therefore lies at neither extreme. The
625 second is that these thresholds are specific to the PL analyzed. Metal content of PL varies widely with feed formulation
626 and supplement source, so the *procedure* (regress final content on inclusion rate, propagate uncertainty, choose an
627 acceptable exceedance probability) transfers, whereas the numerical threshold does not.

628 **4.5 Cd governs risk in a system whose mass is governed by Zn**

629 The ecological risk analysis reframes what “metal contamination” means in this material. On a mass basis, the compost is
630 a Mn, Zn, Cu, and Fe product: these four account for 95% of the trace-metal inventory, and the first three alone for 76%.
631 On a risk basis, it is a Cd product. Cd contributed 81–84% of the potential ecological risk index in the PL-rich treatments
632 while accounting for 0.3% of the trace-metal mass, because its toxic-response weighting exceeds that of Zn thirty-fold.

633 The soil-accumulation model sharpens the same point into a management horizon. Continuous application of the pure-PL
634 compost at a routine rate would carry plow-layer Cd to the Directive 86/278/EEC limit within a single professional career,

635 whereas the VW-rich blends push that horizon beyond any meaningful planning interval. Because the model omits
636 leaching, plant offtake and erosion, these are conservative upper bounds on the time available; the true intervals will be
637 somewhat longer, but the two-order-of-magnitude contrast between blends is robust to those omissions.

638 Taken with the liberation result, the practical message is compounding rather than merely additive. Not only does PL-rich
639 compost carry the highest Cd load, but that load is also the one most likely to be under-reported if the product is sampled
640 before it is mature.

641 **4.6 Dietary Cd is the health endpoint that the sampling defect reaches**

642 The risk index of Sect. 4.5 is ecological. The endpoint that connects this geochemistry to human health is dietary Cd, and
643 the chain linking them is worth stating explicitly.

644 Cd has among the highest soil-to-plant transfer coefficients of any trace metal, and across Europe cereals and leafy
645 vegetables, rather than meat or fish, are the dominant dietary source (Kabata-Pendias, 2011; Smith, 2009). The European
646 Food Safety Authority set a tolerable weekly intake of 2.5 μg per kilogram of body weight, and mean adult exposure in
647 Europe sits close to that value, with vegetarians reaching roughly twice it (European Food Safety Authority, 2009). The
648 population therefore has little headroom, and a compost destined for vegetable production sits squarely on the pathway that
649 matters.

650 The soil-accumulation model can be carried one step further, to the crop. Cd soil-to-plant transfer coefficients for leafy
651 vegetables span roughly 1 to 10 on a dry-matter basis, the value rising with decreasing pH (Kabata-Pendias, 2011). At the
652 plow-layer concentration of 1.0 mg kg^{-1} that continuous application of the pure-PL compost would reach, and taking leafy
653 vegetables to be about 90% water, the resulting fresh-weight Cd content is 0.10 mg kg^{-1} at a transfer coefficient of 1, 0.20
654 at 2, 0.50 at 5 and 1.00 at 10. The maximum levels set for Cd in vegetables by Regulation (EU) 2023/915 span 0.02 to 0.50
655 mg kg^{-1} wet weight according to the crop (European Commission, 2023). A transfer coefficient above about 2 therefore
656 places the produce within the regulated band, and one of 5 or more at its upper limit. The calculation is deliberately
657 transparent rather than precise: it assumes a single crop type, a fixed moisture content and a transfer coefficient that in
658 reality varies by an order of magnitude with soil pH and OM. Its purpose is to show that the soil limit and the food limit
659 are separated by a factor that is small and uncertain, not by a comfortable margin.

660 That uncertainty runs in an unhelpful direction here. The VW-rich blends that carry the least Cd are also the most acidic
661 (Sect. 3.11), and transfer coefficients rise as pH falls, so part of the benefit of dilution is returned through increased
662 availability of the Cd that remains.

663 Three features of the present result bear on that pathway. First, dilution moves the total Cd burden in the right direction,
664 since the blends carrying the least Cd are the ones richest in VW, but not without cost, because those same blends are the
665 most saline and the most acidic, which is why the operating point recommended in Sect. 4.4 lies below the VW-rich
666 extreme rather than at it. Second, the soil-accumulation horizon for the pure-PL product, 46 years to carry the plow layer
667 from a background of 0.41 to the 1.0 mg kg^{-1} limit, is shorter than the working life of a field, and the plow layer does not
668 reset. Third, and most consequentially, the sampling defect errs in the unsafe direction: a producer sampling at 15 days
669 obtains a compliant result for a material that a mature-product measurement would have excluded, and that material is then
670 applied to food crops at a rate the regulation exists to prevent.

671 That is the practical weight of a result which is, at bottom, analytical. Whether the Cd in a compost is visible to the
672 regulatory digestion determines whether the product reaches a vegetable field, and how much of it does.

673 **4.7 Limitations of the design and of the models**

674 Several constraints bound the strength of these conclusions, and we state them explicitly.

675 **Replication structure.** Each treatment occupied a single pit, and the three replicates per sampling occasion are composite
676 samples drawn from that pit rather than independent experimental units. Treatment effects are consequently confounded
677 with pit effects, and the error term estimates sampling and analytical variability rather than true experimental error.
678 Probability values attaching to between-treatment comparisons should therefore be read descriptively, and the dose–
679 response regressions as characterizing these particular piles rather than the treatments in the abstract. The central result of
680 this paper is unaffected by this limitation, because the liberation analysis is a within-pile temporal comparison in which
681 each pile serves as its own control, and because the group contrast is between elements measured in the same digests.

682 **Unrecovered error terms.** No validated error term could be obtained for Cr, Cd, or Pb, precisely the elements central to
683 the main finding. The conclusion accordingly rests on effect magnitude, 2.2- to 17.8-fold changes against a ceiling of 2.0-
684 fold, and on information-theoretic model comparison, rather than on formal significance testing.

685 **Non-independent units in the group contrast.** The Mann–Whitney contrast treats element $\times$ treatment combinations, not
686 replicates, as units, and each element contributes one value to every treatment, so the 21 units are not mutually
687 independent, and the probability attaching to them is optimistic. The element-level contrast reported in Sect. 3.2 removes
688 that dependence but leaves only seven units, a number at which no test can return a probability below 0.057, however
689 complete the separation. Neither version of the test is therefore load-bearing on its own, which is why the argument is built
690 on the mass-loss ceiling, on the robustness of Λ across scenarios and on model comparison instead. The bootstrap intervals
691 resample the same units and inherit the same dependence, so they too should be read as describing the observed set of
692 elements rather than a wider population.

693 **Small-sample model comparison.** Each series comprises six observations and the liberation model carries three
694 parameters, so the correction term of the small-sample criterion is divided by $n - K - 1 = 2$. AIC_c remains defined but is at
695 the edge of its useful range, and the Δ AIC_c values should be read as ranking the two models rather than as calibrated
696 evidence ratios.

697 **Dry-matter loss not measured.** Pile mass was not tracked gravimetrically, so λ is inferred rather than determined. This is
698 the reason for the three-scenario design, and the central conclusion is demonstrably robust across the whole range; but a
699 direct gravimetric measurement would convert Λ from a bounded inference into a point estimate.

700 **Pseudo-total speciation only.** No sequential extraction was performed, so the proposed liberation mechanism is inferred
701 by elimination rather than observed directly, and no statement about bioavailability is possible from these data.

702 **Age of the dataset.** The trial was run in 2009, and the primary concentrations were first reported in an institutional thesis
703 (Manzoor, 2010). The central finding is a property of the analytical method rather than of that particular season: a nitric–
704 perchloric digestion recovers a matrix-dependent fraction of the metal inventory, and that dependence does not expire with
705 the sample. The absolute concentrations are the perishable part. Statutory ceilings on zinc in compound feed have since
706 been lowered: Regulation (EU) 2016/1095 caps zinc at 120 mg kg⁻¹ of complete feed for poultry (European Commission,
707 2016), so litter produced today under comparable regulation would carry a lower Zn burden, and the blending thresholds
708 derived here should be recomputed for the litter actually in use rather than transferred.

709 **Single site, single season, single feedstock source.** Absolute concentrations are not transferable, since PL metal content
710 varies with feed formulation. The generalizable claim is the *behavior*, divergent liberation between metal classes, and it
711 requires independent replication across feedstocks and climates.

712 **Total rather than hexavalent Cr.** Only total Cr was determined, so no compliance statement is possible for Cr, and the
713 Cr liberation result cannot be attributed to a particular oxidation state.

714 **Model simplifications.** The soil-accumulation model assumes linear accumulation with no losses and a fixed plow-layer
715 mass; the Monte-Carlo model propagates the uncertainty of the fitted mean together with a multiplicative analytical error
716 of constant CV. It therefore answers what the expected Cd content of a blend is, not what a single future batch will assay:
717 adding the residual between-pile variance as a prediction rather than a confidence problem would move the 5% threshold
718 from 37% to 28% PL, so the value quoted here is the less cautious of the two. Both are transparent approximations chosen
719 for interpretability rather than realism, and both are conservative in the direction that matters.

720 **4.8 A three-route digestion experiment would settle the mechanism**

721 One experiment would convert the central inference from elimination to demonstration. A composting time series should
722 be analyzed in parallel by three routes: BCR three-step sequential extraction (Rauret et al., 1999), the conventional pseudo-
723 total digestion used here, and a genuinely total digestion incorporating hydrofluoric acid. The model makes a sharp
724 prediction. Total content should remain constant; pseudo-total content should rise; and the rise should be quantitatively
725 accounted for by the transfer of metal out of the BCR residual fraction. Gravimetric tracking of pile mass, together with a
726 certified reference material carried through every batch, would close the remaining degrees of freedom. If the prediction
727 holds, the implication for compost regulation is immediate and general.

5 Conclusions

1. Mature-product concentrations of every element except Fe scaled linearly with the PL fraction of the feedstock, indicating simple mixing behavior and allowing final metal load to be predicted from feedstock composition alone. Fe, uniquely enriched in the VW endmember through adhering soil, serves as an internal tracer of mineral input.
2. Elements separated into two non-overlapping behavioral classes. Zn, Cu, Fe, Mn and Ni enriched by 1.02–1.45 fold over the cycle, consistent with matrix dry-matter loss. Cr, Cd and Pb enriched by 2.2–29 fold, which matrix loss cannot produce.
3. A mass-conservative partition model resolved each trajectory into a matrix-loss term and a liberation term. The conservative set returned a liberation factor of 1.03, the toxic set 5.11 ($P = 1.4 \times 10^{-4}$), and the separation persisted even when dry-matter loss was forced to a physically inadmissible 50% ($\Lambda = 2.78$). Mineral ingress, bounded at 0.13% w/w by the Fe signal, accounts for about 4% of the Cr rise, under 1% of the Pb rise, and cannot in principle explain the Cd rise.
4. Liberation followed first-order kinetics with $k = 0.0143 \text{ d}^{-1}$ and a half-time of 49 days, placing the process squarely within a normal composting cycle. The measured increase in Cr, Cd and Pb is therefore best explained by rising analytical recovery from a humifying matrix rather than by accumulation.
5. The compliance verdict for an unchanged pile consequently inverts across the cycle: pure-PL compost reports Cd as compliant at 15 days and at 2.2 times the EU limit at 90 days. Compliance sampling should be tied to an independent maturity criterion, and regulatory protocols should specify near-total digestion.
6. Cd was the sole binding constraint under Regulation (EU) 2019/1009 and contributed 81–84% of the potential ecological risk index in PL-rich treatments. Monte-Carlo analysis places the PL share at which exceedance risk reaches 5% at 37%; at routine application rates, this choice moves the horizon for reaching the soil Cd limit from 46 years to roughly two millennia.

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Consent to participate / Consent to publish. Not applicable.

Data availability. The complete dataset is provided as Supplementary Material in three open formats: a tidy long-form CSV of 420 records giving every treatment mean, its standard error and the provenance of that error; a wide-form CSV; and an Excel workbook containing the data together with every derived table in this paper. The digitized source file records the provenance of each block, including the error mean squares and coefficients of variation published in the original analysis-of-variance tables. No value in the archive is simulated, imputed or interpolated. Part of the primary concentration dataset was reported previously in an institutional thesis (Manzoor, 2010); the modeling framework, the partition analysis, the kinetic treatment, the compliance and risk models and all interpretations are original to this work. The archive will be deposited in a public repository with a permanent DOI on acceptance.

Code availability. The analysis code is provided as Supplementary Material: the partition model and liberation factors, the liberation kinetics, the Monte-Carlo compliance model, the soil-accumulation model, the geochemical indices, the model comparison and bootstrap intervals, the ordination, and the scripts that draw Figures 1–7. The statistical routines are implemented from first principles, so results do not depend on the version of any third-party statistics library; NumPy and Matplotlib are the only external requirements, and all random draws are seeded, so the Monte-Carlo and bootstrap results reproduce exactly. The code will be deposited with the data on acceptance.

772 **Compliance with ethical standards.** All authors have read, understood, and have complied as applicable with the
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774 **Author contributions.** A. Manzoor: conceptualization, investigation, data curation, formal analysis, modeling,
775 visualization, and writing of the original draft. M. Manzoor: assistance with the composting experiment and the associated
776 field activities, and critical review of the manuscript. A. Aamir: assistance with the data analysis and with the
777 implementation of the models, and contribution to the writing of the manuscript. T. Alam: methodology, validation, and
778 critical revision of the manuscript. A. N. Chaudhry: supervision, methodology, validation, and critical revision of the
779 manuscript. All authors read and approved the final manuscript.

780 **References**

781 Amir, S., Hafidi, M., Merlina, G., & Revel, J.-C. (2005). Sequential extraction of heavy metals during composting of
782 sewage sludge. *Chemosphere*, 59(6), 801–810. <https://doi.org/10.1016/j.chemosphere.2004.11.016>

783 Anderson, J. M., & Ingram, J. S. I. (1993). *Tropical soil biology and fertility: A handbook of methods* (2nd ed.). CAB
784 International.

785 Bernal, M. P., Albuquerque, J. A., & Moral, R. (2009). Composting of animal manures and chemical criteria for compost
786 maturity assessment. A review. *Bioresource Technology*, 100(22), 5444–5453.
787 <https://doi.org/10.1016/j.biortech.2008.11.027>

788 Bolan, N. S., Szogi, A. A., Chuasavathi, T., Seshadri, B., Rothrock, M. J., & Panneerselvam, P. (2010). Uses and
789 management of poultry litter. *World's Poultry Science Journal*, 66(4), 673–698.
790 <https://doi.org/10.1017/S0043933910000656>

791 Burnham, K. P., & Anderson, D. R. (2002). *Model selection and multimodel inference: A practical information-theoretic*
792 *approach* (2nd ed.). Springer.

793 Council of the European Communities. (1986). Council Directive 86/278/EEC on the protection of the environment, and in
794 particular of the soil, when sewage sludge is used in agriculture. *Official Journal of the European Communities*, L181, 6–
795 12.

796 European Commission. (2016). Commission Implementing Regulation (EU) 2016/1095 concerning the authorisation of
797 zinc compounds as feed additives for all animal species. *Official Journal of the European Union*, L182, 7–27.

798 European Commission. (2023). Commission Regulation (EU) 2023/915 of 25 April 2023 on maximum levels for certain
799 contaminants in food and repealing Regulation (EC) No 1881/2006. *Official Journal of the European Union*, L119, 103–
800 157.

801 European Food Safety Authority. (2009). Cadmium in food — Scientific opinion of the Panel on Contaminants in the
802 Food Chain. *EFSA Journal*, 7(3), 980. <https://doi.org/10.2903/j.efsa.2009.980>

803 European Parliament and Council. (2019). Regulation (EU) 2019/1009 laying down rules on the making available on the
804 market of EU fertilising products. *Official Journal of the European Union*, L170, 1–114.

805 Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. *Water*
806 *Research*, 14(8), 975–1001. [https://doi.org/10.1016/0043-1354\(80\)90143-8](https://doi.org/10.1016/0043-1354(80)90143-8)

807 He, M., Tian, G., & Liang, X. (2009). Phytotoxicity and speciation of copper, zinc and lead during the aerobic composting
808 of sewage sludge. *Journal of Hazardous Materials*, 163(2–3), 671–677. <https://doi.org/10.1016/j.jhazmat.2008.07.013>

809 Hseu, Z.-Y. (2004). Evaluating heavy metal contents in nine composts using four digestion methods. *Bioresource*
810 *Technology*, 95(1), 53–59. <https://doi.org/10.1016/j.biortech.2004.02.008>

811 Hsu, J.-H., & Lo, S.-L. (2001). Effect of composting on characterization and leaching of copper, manganese, and zinc from
812 swine manure. *Environmental Pollution*, 114(1), 119–127. [https://doi.org/10.1016/S0269-7491\(00\)00198-6](https://doi.org/10.1016/S0269-7491(00)00198-6)

- Isaac, R. A., & Johnson, W. C. (1975). Collaborative study of wet and dry ashing techniques for the elemental analysis of plant tissue by atomic absorption spectrophotometry. *Journal of the Association of Official Analytical Chemists*, 58(3), 436–440. <https://doi.org/10.1093/jaoac/58.3.436>
- Kabata-Pendias, A. (2011). *Trace elements in soils and plants* (4th ed.). CRC Press.
- Liu, Y., Ma, L., Li, Y., & Zheng, L. (2007). Evolution of heavy metal speciation during the aerobic composting process of sewage sludge. *Chemosphere*, 67(5), 1025–1032. <https://doi.org/10.1016/j.chemosphere.2006.10.056>
- Manzoor, A. (2010). *Assessment of heavy metal availability during co-composting of poultry litter and vegetable waste* [Unpublished MSc (Hons) thesis]. Department of Soil Science and Soil & Water Conservation, PMAS–Arid Agriculture University, Rawalpindi.
- Müller, G. (1969). Index of geoaccumulation in sediments of the Rhine River. *GeoJournal*, 2, 108–118.
- Nicholson, F. A., Chambers, B. J., Williams, J. R., & Unwin, R. J. (1999). Heavy metal contents of livestock feeds and animal manures in England and Wales. *Bioresource Technology*, 70(1), 23–31. [https://doi.org/10.1016/S0960-8524\(99\)00017-6](https://doi.org/10.1016/S0960-8524(99)00017-6)
- Paré, T., Dinel, H., Schnitzer, M., & Dumontet, S. (1998). Transformations of carbon and nitrogen during composting of animal manure and shredded paper. *Biology and Fertility of Soils*, 26(3), 173–178. <https://doi.org/10.1007/s003740050364>
- Rauret, G., López-Sánchez, J. F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., & Quevauviller, P. (1999). Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *Journal of Environmental Monitoring*, 1(1), 57–61. <https://doi.org/10.1039/a807854h>
- Smith, S. R. (2009). A critical review of the bioavailability and impacts of heavy metals in municipal solid waste composts compared to sewage sludge. *Environment International*, 35(1), 142–156. <https://doi.org/10.1016/j.envint.2008.06.009>
- Tomlinson, D. L., Wilson, J. G., Harris, C. R., & Jeffrey, D. W. (1980). Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoländer Meeresuntersuchungen*, 33(1–4), 566–575. <https://doi.org/10.1007/BF02414780>
- US Environmental Protection Agency. (1993). *Standards for the use or disposal of sewage sludge* (40 CFR Part 503). US Government Printing Office.
- Woodbury, P. B. (1992). Trace elements in municipal solid waste composts: A review of potential detrimental effects on plants, soil biota, and water quality. *Biomass and Bioenergy*, 3(3–4), 239–259. [https://doi.org/10.1016/0961-9534\(92\)90029-P](https://doi.org/10.1016/0961-9534(92)90029-P)
- Zheng, G. D., Gao, D., Chen, T. B., & Luo, W. (2007). Stabilization of nickel and chromium in sewage sludge during aerobic composting. *Journal of Hazardous Materials*, 142(1–2), 216–221. <https://doi.org/10.1016/j.jhazmat.2006.08.003>

Supplementary Table S1

Treatment means $\pm$ 1 SE (mg kg⁻¹ dry matter). Standard errors are derived as the square root of MS_{error}/3. Values for Cr, Cd and Pb are reported without standard errors because no error term could be validated (Sect. 2.4).

Zn

PL:VW	15 d	30 d	45 d	60 d	75 d	90 d
T1 (100:0)	199.06 $\pm$ 6.92	200.00 $\pm$ 7.41	201.00 $\pm$ 8.08	205.00 $\pm$ 6.44	211.00 $\pm$ 7.58	213.30 $\pm$ 7.94
T2 (75:25)	166.44 $\pm$ 6.92	166.00 $\pm$ 7.41	171.00 $\pm$ 8.08	174.00 $\pm$ 6.44	177.00 $\pm$ 7.58	178.92 $\pm$ 7.94
T3 (50:50)	106.74 $\pm$ 6.92	107.00 $\pm$ 7.41	109.00 $\pm$ 8.08	106.00 $\pm$ 6.44	108.96 $\pm$ 7.58	109.08 $\pm$ 7.94
T4 (25:75)	64.41 $\pm$ 6.92	65.00 $\pm$ 7.41	67.00 $\pm$ 8.08	69.00 $\pm$ 6.44	71.96 $\pm$ 7.58	74.44 $\pm$ 7.94
T5 (0:100)	38.26 $\pm$ 6.92	39.00 $\pm$ 7.41	41.00 $\pm$ 8.08	44.00 $\pm$ 6.44	47.98 $\pm$ 7.58	50.17 $\pm$ 7.94

Cu

PL:VW	15 d	30 d	45 d	60 d	75 d	90 d
T1 (100:0)	193.72 ± 6.45	195.67 ± 5.06	206.34 ± 3.91	208.45 ± 4.72	209.24 ± 2.63	211.30 ± 2.42
T2 (75:25)	123.45 ± 6.45	121.53 ± 5.06	131.96 ± 3.91	134.20 ± 4.72	135.45 ± 2.63	136.35 ± 2.42
T3 (50:50)	98.61 ± 6.45	102.60 ± 5.06	111.01 ± 3.91	115.40 ± 4.72	117.24 ± 2.63	117.50 ± 2.42
T4 (25:75)	65.57 ± 6.45	69.53 ± 5.06	74.64 ± 3.91	81.47 ± 4.72	82.96 ± 2.63	84.44 ± 2.42
T5 (0:100)	49.90 ± 6.45	50.96 ± 5.06	54.79 ± 3.91	56.69 ± 4.72	61.34 ± 2.63	62.37 ± 2.42

848 **Fe**

PL:VW	15 d	30 d	45 d	60 d	75 d	90 d
T1 (100:0)	158.68 ± 1.66	159.46 ± 2.14	170.01 ± 1.36	185.01 ± 4.97	201.11 ± 1.35	204.52 ± 1.91
T2 (75:25)	171.57 ± 1.66	172.98 ± 2.14	181.45 ± 1.36	195.98 ± 4.97	209.46 ± 1.35	211.50 ± 1.91
T3 (50:50)	186.01 ± 1.66	193.34 ± 2.14	213.24 ± 1.36	228.89 ± 4.97	239.48 ± 1.35	255.18 ± 1.91
T4 (25:75)	198.74 ± 1.66	198.89 ± 2.14	205.30 ± 1.36	223.36 ± 4.97	234.16 ± 1.35	244.32 ± 1.91
T5 (0:100)	214.35 ± 1.66	216.61 ± 2.14	223.33 ± 1.36	236.49 ± 4.97	245.39 ± 1.35	230.94 ± 1.91

849 **Mn**

PL:VW	15 d	30 d	45 d	60 d	75 d	90 d
T1 (100:0)	375.01 ± 2.51	375.89 ± 4.09	380.00 ± 3.97	383.47 ± 51.63	384.93 ± 3.66	388.36 ± 4.34
T2 (75:25)	283.73 ± 2.51	283.56 ± 4.09	290.45 ± 3.97	292.76 ± 51.63	296.45 ± 3.66	300.62 ± 4.34
T3 (50:50)	193.19 ± 2.51	195.46 ± 4.09	200.55 ± 3.97	203.66 ± 51.63	205.00 ± 3.66	207.18 ± 4.34
T4 (25:75)	135.24 ± 2.51	136.22 ± 4.09	141.61 ± 3.97	139.46 ± 51.63	140.66 ± 3.66	142.77 ± 4.34
T5 (0:100)	115.79 ± 2.51	118.66 ± 4.09	123.46 ± 3.97	123.00 ± 51.63	124.56 ± 3.66	120.95 ± 4.34

850 **Ni**

PL:VW	15 d	30 d	45 d	60 d	75 d	90 d
T1 (100:0)	35.75 ± 0.58	36.55 ± 0.37	40.46 ± 0.38	41.65 ± 0.66	40.88 ± 0.89	41.55 ± 0.72
T2 (75:25)	27.83 ± 0.58	27.68 ± 0.37	31.58 ± 0.38	32.14 ± 0.66	33.01 ± 0.89	33.10 ± 0.72
T3 (50:50)	18.75 ± 0.58	19.15 ± 0.37	23.15 ± 0.38	23.48 ± 0.66	24.10 ± 0.89	25.00 ± 0.72
T4 (25:75)	9.70 ± 0.58	10.11 ± 0.37	12.35 ± 0.38	13.22 ± 0.66	13.64 ± 0.89	14.11 ± 0.72
T5 (0:100)	4.65 ± 0.58	4.87 ± 0.37	4.89 ± 0.38	5.14 ± 0.66	5.99 ± 0.89	6.19 ± 0.72

851 **Cr**

PL:VW	15 d	30 d	45 d	60 d	75 d	90 d
T1 (100:0)	0.57	0.88	1.43	1.99	2.49	2.51
T2 (75:25)	0.49	0.65	0.99	1.53	2.17	2.26
T3 (50:50)	0.28	0.46	0.83	1.36	1.84	2.03
T4 (25:75)	0.07	0.079	0.09	0.23	0.79	0.84
T5 (0:100)	0.02	0.05	0.086	0.14	0.67	0.58

852 **Cd**

PL:VW	15 d	30 d	45 d	60 d	75 d	90 d
T1 (100:0)	0.84	1.25	1.86	2.69	3.28	3.34
T2 (75:25)	0.49	0.86	1.27	1.67	2.03	2.29

T3 (50:50)	0.09	0.47	0.78	1.15	1.59	1.6
T4 (25:75)	0.006	0.009	0.031	0.056	0.077	0.078
T5 (0:100)	0.003	0.006	0.009	0.03	0.05	0.06

853 **Pb**

PL:VW	15 d	30 d	45 d	60 d	75 d	90 d
T1 (100:0)	4.45	5.82	6.95	8.74	9.66	9.85
T2 (75:25)	3.33	3.79	4.94	6.31	7.01	7.21
T3 (50:50)	2.25	2.61	4.47	5.34	6.67	6.68
T4 (25:75)	0.78	0.99	1.25	1.72	1.95	2.22
T5 (0:100)	0.52	0.89	1.15	1.54	1.87	2.05

854 **Supplementary Table S2**

855 Within-occasion CV (%) for each element at each sampling date. Where an error mean square was archived, the
856 coefficient is recovered as 100 times the square root of MS_{error} , divided by the grand mean of that occasion; for Cr and Cd
857 the coefficients were tabulated directly in the original record. Median is the median across the six occasions. The isolated
858 large values, Mn at 60 d, Cr at 90 d, and Cd at 75 and 90 d, are retained rather than trimmed. No precision figure of any
859 kind survives for Pb, and no certified reference material was analyzed, so trueness cannot be established (Sect. 2.3).

Element	15 d	30 d	45 d	60 d	75 d	90 d	Median	Source
Zn	10.4	11.1	11.9	9.3	10.6	11.0	10.8	recovered from MS_{error}
Cu	10.5	8.1	5.8	6.9	3.8	3.4	6.4	recovered from MS_{error}
Fe	1.5	2.0	1.2	4.0	1.0	1.4	1.5	recovered from MS_{error}
Mn	2.0	3.2	3.0	39.1	2.8	3.2	3.1	recovered from MS_{error}
Ni	5.2	3.2	2.9	4.9	6.6	5.2	5.0	recovered from MS_{error}
Cr	9.1	1.0	1.1	1.4	0.8	17.7	1.2	tabulated in the original record
Cd	1.3	1.3	1.4	1.5	20.8	20.7	1.4	tabulated in the original record
Pb	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	none available

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Supplementary Files

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