

An ultrasound accelerated sequential extraction method and its application for element partitioning studies in compost from mixed waste streams

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A rapid ultrasound accelerated sequential extraction procedure is presented which is modified from the standard BCR protocol and validated using the BCR 601 reference material. The method is accelerated at the extraction steps: for example, in the standard method each extraction step takes 16 h whereas with the ultrasonic extraction method developed in this work each step took 15 min. This means a further step can be included in the protocol without greatly increasing the experimental time. An extraction with pyrophosphate solution was therefore included to provide more information about the interaction between the elements and humic substances during the composting process. The new method has been applied to monitoring the metal partitioning behaviours in a composting process involving mixed waste streams. The metal partitioning profiles obtained from this new method show that in many cases composting tends to redistribute the metals from more labile forms to combined forms, especially to forms combined with humic substances.

Introduction

Heavy metal speciation studies continue to be of great value in environmental monitoring.¹ This is because not only the concentration of the heavy metals but more critically their forms existing in the environment will decide their toxicity, mobility and bioavailability.² Determination of the exact forms of certain elements in natural systems is challenging and time-consuming because the exact species must be identified and that usually requires sophisticated hybrid instrumental techniques. In the case of a solid sample, it becomes more difficult as the original species can easily be changed when trying to dissolve them.

Alternatively, various operationally defined speciation methods have been proposed for the determination of metal behaviour in soil, sediment or other environmental solid materials. These methods are usually based on the sequential extraction of solid samples with various attacking reagents under defined experimental conditions. Among them Tessier's method and the BCR three step sequential extraction method, developed under the auspices of the Community Bureau of Reference (BCR, now the Standard, Measurement and Testing Programme of the Commission of the European Communities), are most extensively exploited.^{3–6} Recently, an improved version of the old BCR method has been published in which a stronger reducing agent is used and a fourth step (an *aqua regia* digestion) incorporated.⁷ One of the great advantages of the BCR methods is that there is a reference material available which enables the quality of the measurements to be controlled. Without proper control of the measurement, the results would be meaningless to environmental studies. In common with other sequential extraction protocols, however, the BCR protocol is very time consuming.

The use of ultrasound power has been investigated to speed up sequential extraction methods because it has long been recognised that the cavitation effect created by ultrasound waves can break down the particle size, exposing a fresh surface and aggressively agitating the solution system.⁸ Despite its potential usefulness, the numbers of publications using ultrasound for extracting heavy metals from solid environmental

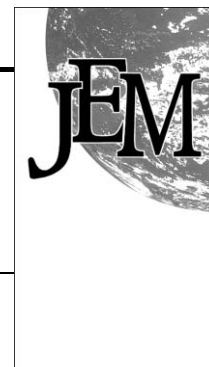
matrices is still very limited. Ashley reviewed the studies of ultrasonic extraction for heavy metal determinations and demonstrated its potential for environmental and industrial hygiene applications.⁹ An ultrasound method based on the old BCR three-step extraction method was applied to the speciation of heavy metals in sewage sludge and sewage sludge-amended soil samples.^{5,10} The effects of ultrasound power and sonication time were found to be significant, and with proper optimisation ultrasound extraction was shown to give results comparable to the conventional method.

In our previous work,¹¹ a modified version of the old BCR three step extraction protocol was applied to the determination of metal partitioning profiles in the composting process. Those results showed that the element partitioning profile changed during the composting process, reflecting physicochemical changes within the compost as it matured. In this paper, ultrasonic power is used to speed up the conventional extraction method. The speed of the new extraction method provides two advantages. Firstly, it allows the composting process to be monitored more frequently, which helps to provide a more detailed understanding of the partitioning behaviour of heavy metals. Secondly, as each step is much less time consuming a further step, designed to look at the proportion of elements combined with humic substances, could be included in the new scheme without adding excessively to the timescales. In this new step the sample is extracted with 0.1 M sodium pyrophosphate solution before the residue is digested with hydrogen peroxide.^{12,13} The novel ultrasonic extraction method was applied to a new municipal compost site with mixed waste streams.

Experimental

Reagents

Super-purity grade reagents (hydrogen peroxide, acetic acid, hydrochloric acid and nitric acid) were purchased from Romil Ltd., Cambridge, UK. Hydroxylamine hydrochloride (98%, A.C.S. reagent) and ammonium acetate (97%, A.C.S. reagent) were purchased from Sigma-Aldrich Co. Ltd.. 0.1 M sodium



pyrophosphate solution was prepared from anhydrous tetrasodium pyrophosphate (Merck, Poole, Dorset, UK). The BCR reference material BCR 601 was purchased from Qmx Laboratories Limited, Essex, UK. All the standard solutions were prepared from $1000 \pm 2 \mu\text{g ml}^{-1}$ of commercial stock standards (Peak Performance, Qmx Laboratories Limited). High purity de-ionised water (18 M Ω cm resistivity) was obtained from an Elgstat UHQ PS System (Elga, High Wycombe, UK).

Procedures and instrumentation

The sequential extraction steps employed in this paper was similar to the one described in our previous paper¹¹ except that the procedure included the extra extraction step with 0.1 M sodium pyrophosphate solution before digestion with hydrogen peroxide. A summary of reagents used in each step is given in Table 1. To be able to work with the microwave digestion system all the extractions were carried out on 0.5 g of solid sample and the amount of extraction solutions was half of that described in the standard protocol.⁴ The ultrasonic extraction was carried out with an Ultrasonic Liquid Processor (MISONIX, XL-2020, Farmingdale, USA). The sonicator was fitted with either a standard probe or a dual horns system and it was operated either in a pulse or a continuous mode. 50 ml acid washed glass centrifuge tubes were used for the probe extraction experiment to ensure the maximum reflection of the ultrasound waves. For the purpose of comparison, the conventional extraction was also carried out with a horizontal flask shaker (Model SF1, Stuart Scientific, UK). A centrifuge was used to separate the supernatant from the sample extracts (1040 Centurion Scientific, UK) and the total digestion of the compost samples was achieved using a microwave digestion system (CEM Corporation, MDS 2100, USA). All the solutions obtained were transferred to 50 ml polyethylene tubes (Bibby Sterilin Ltd., UK) and stored at 2 °C in a cold room before analysis. The analysis of the extracted solution was carried out by ICP atomic emission spectrometry (PerkinElmer Plasma 40, Beaconsfield, Buckinghamshire, UK) or ICP mass spectrometry (ThermoElemental, Winsford, Cheshire, UK) depending on the element concentrations. Reagent matched standards were used as described previously.¹¹

The temperature of the composting system was measured *in situ* at each sampling point by using a temperature probe (RS 206-3722 Thermocouple, Taiwan). A pH meter (Fisherbrand Hydrus 500 pH Meter, Fisher Scientific UK Ltd., Loughborough) was used to determine the pH values of the samples.

Sampling of compost and sample preparation

An open-air windrow-composting system was chosen in this study. The starting materials were more mixed than the green waste starting material used for the results reported previously and consisted of shredded old building wood, straw and other vegetable waste. The windrow was turned once per week during the active stage and it was watered when necessary to maintain the moisture content. Once the compost was deemed to be mature (about 2 months) the compost pile was moved to an open field and left without further turning. Three representative samples, of about 1 kg each in wet weight, were taken randomly along the windrow at a depth about 50 cm from the surface. Sampling was more frequent during the first few weeks,

especially at the initial stages, and less frequent afterwards, since changes were much slower once the compost was mature. The temperature was recorded *in situ* and the pH was measured in the laboratory in a mixture of 1 g air dried sample and 10 ml water. Sampling at this composting site lasted for 5 months. On returning to the laboratory, the wet samples were spread onto plastic trays in fume cupboards and allowed to dry at ambient temperature. Very occasionally large pieces of stones or metals were seen in the samples and these were picked out manually before the samples were further homogenized. Liquid nitrogen was added when grinding the sample with a mortar and pestle, as this could make the sample more brittle and kept the grinding process free from dust. After initial grinding the samples were passed through a 3 mm sieve and then a quarter of its original amount was taken to be a representative sample. It was further ground to pass a 1 mm sieve and again the sample was reduced by a quarter. Then approximately the same amount of each of the three samples for each day were mixed and homogenized to make a representative sample for that sampling day. These final samples were kept in labelled envelopes at ambient temperature before analysis.

Results and discussions

Study of ultrasound extraction with BCR reference material BCR 601

The BCR reference material BCR 601 was used to validate the ultrasonic method. In this work a probe system was utilised for ultrasonic extraction as opposed to an ultrasound bath. Previously the use of an ultrasonic baths has been reported⁵ because several samples can be processed at once, however the power available is lower and less directed. In preliminary experiments in this work it was found that acceptable extraction results could not be obtained for BCR601 using the ultrasonic bath.

To investigate the importance of the different variables, preliminary experiments were carried out comparing the concentrations of the metals extracted in the first step with the certified values. The maximum power output for the instrument was 500 W and, in this experiment, an intermediate output power (power setting at 5) was used in either a continuous mode or a pulse mode. As reported by previous workers^{5,10} the length of time for sonication and the power used was important. These conditions were a compromise, designed to give maximum extraction in the shortest possible time, whilst avoiding an increase in the temperature of the sample. When the sonicator was running in continuous mode, the temperature of the extracting solution increased steadily and over the 15 min processing time the temperature of the 20 ml aliquot of solution could easily reach 70 °C. This should be avoided in the experiment, as the increase in temperature can change the chemical equilibrium of the extraction solutions. Cooling the sample tube with an ice water bath or choosing the pulse mode for the extraction can overcome this problem. In our experiment, the cooling method was chosen as this could reduce the overall extraction time. The use of a standard single probe was found to have no significant differences as compared with the dual horn system, hence the dual horn system was used in the rest of the experiment as this can

Table 1 The sequential extraction scheme for the element partitioning study in compost

Extracting reagent		Nominal target phases
Step 1	0.11 mol l ⁻¹ acetic acid	Exchangeable, acid and water soluble
Step 2	0.1 mol l ⁻¹ hydroxylamine hydrochloride	Reducible
Step 3	0.1 mol l ⁻¹ sodium pyrophosphate	Combined with humic acid
Step 4	Hydrogen peroxide, 1.0 mol l ⁻¹ ammonium acetate	Oxidisable
Step 5	Concentrated HNO ₃	Residual

Table 2 Comparison of results obtained from ultrasound extraction (UE) with that obtained by the conventional extraction method and the certified values of reference material BCR 601. The values are given in mg kg⁻¹

Element		UE values (<i>n</i> = 6)	Conventional values (<i>n</i> = 6)	Certified values ¹⁷
Step 1	Cr	0.38 ± 0.07	0.34 ± 0.06	0.36 ± 0.04
	Ni	7.62 ± 1.02	8.45 ± 0.80	8.01 ± 0.73
	Zn	239 ± 6	233 ± 8	264 ± 5
	Cd	2.81 ± 0.33	4.06 ± 0.16	4.14 ± 0.23
	Pb	2.91 ± 0.16	2.89 ± 0.17	2.68 ± 0.35
Step 2	Ni	5.98 ± 0.16	6.61 ± 0.90	6.05 ± 1.09
	Zn	178 ± 10	180 ± 15	182 ± 11
	Cd	3.27 ± 0.56	3.13 ± 0.43	3.08 ± 0.17
Step 3	Ni	7.04 ± 0.70	8.85 ± 1.10	8.55 ± 1.04
	Cd	1.66 ± 0.15	2.5 ± 0.24	1.83 ± 0.20
	Pb	102 ± 6	108 ± 11	109 ± 13

process two samples at the same time. The depth to which the probe was inserted into the centrifuge tube significantly affected the extraction efficiency. The results obtained when the probe was inserted by more than 3 cm in depth into the extraction solution were significantly higher than those obtained at 1 cm depth. This can be explained by the fact that the mixture is not homogenous, there is solid sample and extraction solution in the tube. When the probe is too far away from the sample in the centrifuge tube the ultrasound wave is attenuated too quickly and does not reach the solid sample. Another contributing factor may be that the ultrasound is emitted from the full probe depth, not just the bottom of the probe, and therefore an insertion depth of 3 cm of the probe was chosen for the rest of experiment.

After optimising the parameters of the sonicator, the full extraction experiment was carried out on the BCR601 sample. The results are given in Table 2. As we can see from Table 2, with the exceptions of Cd in step 1 and step 3 and Zn in step 1, the results obtained by the ultrasound extraction were very close to that of conventional method as well as those of certified values. When comparing these results with those reported by other authors,⁵ the difference in Zn content is significant, which may be explained by the use of a different sonicator and probe. The reproducibility of the ultrasound extraction was also comparable to that of conventional method.

The basic characteristics of the compost system

Temperature and pH. The change in temperature and pH in the whole composting process is shown in Fig. 1. Temperature

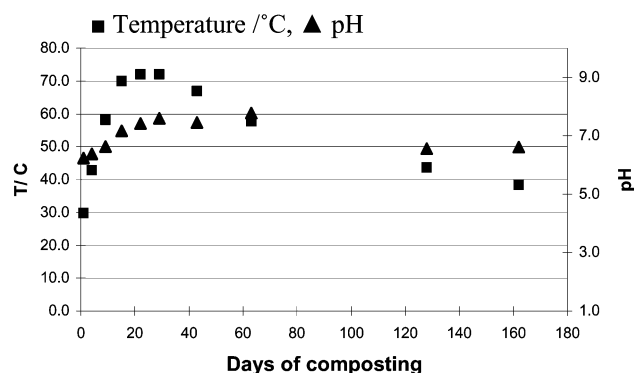


Fig. 1 The change in temperature and pH during the composting process.

Table 3 The total element content in the mature compost. The data is expressed as mg kg⁻¹ in air-dried sample at the 90% confidence interval. "na" in the table refers to the non-availability of the data

Element	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
Compost	43.4 ± 6.6	281 ± 25	5670 ± 524	3.57 ± 0.84	22.1 ± 4.6	85.7 ± 11.1	409 ± 35	10.1 ± 2.8	1.62 ± 0.28	499 ± 34
Standard ¹⁴	100	na	na	na	50	200	400	na	1.5	150

can be a simple indicator for the intensity of the bioorganism activities. It increased rapidly in the first two weeks of composting, then levelled off at about 70 °C for another three weeks and finally began to drop gradually after 5–6 weeks of intensive composting. It is interesting to note that even after three months of maturity in an open field, the temperature of the compost pile stayed as high as 38 °C in the winter in Northern England, which shows that the biodegradation is continuing at a reasonably high level. The pH reflects the change in the chemical nature of the materials being composted. It increases as composting progresses, because of the consumption of organic acid. Once the compost was deemed mature and was not managed the pH dropped again: this was probably because there was not enough oxygen to oxidise the continuously accumulated organic acid to carbon dioxide.

Total element content in the compost. The elemental totals were obtained for 10 selected elements using either ICP-MS or ICP-AES after digestion with nitric acid. Nitric acid was used instead of *aqua regia*⁷ in this experiment because preliminary comparison experiments gave similar extraction results for compost samples. Nitric acid was therefore preferable because *aqua regia* would add chloride to the matrix, which would interfere with As and Cr determination by quadrupole ICP-MS. The detailed procedures are the same as that described in the previous paper.¹¹ As expected, the overall element content increases steadily because of the loss of organic materials in the composting process. For example, the initial content of Pb was measured to be 431 mg kg⁻¹ but, at the end of composting, this figure had reached 499 mg kg⁻¹. With this data, even taking into account the uncertainty in the measurement (Table 3), an overall increase was demonstrated. The elemental content for the last samples (mature compost) is compared with the British Composting Association guidelines¹⁴ for compost given in Table 3. Compared to the compost systems previously reported,¹¹ this system has a much higher metal content. For example, the lead content in the mature compost is three times greater than the upper guideline level for agricultural application. This high content of lead could be due to paint on old building materials.

Comparison of the ultrasound and conventional extraction results on compost samples. To compare the ultrasound method with the conventional shaking procedure for the compost matrix both extraction methods were applied to the compost sample for day 1. Table 4 shows that in most cases

Table 4 Comparison of the extraction results obtained by the ultrasound method with the conventional method on compost samples from day 1. Results expressed as % of total extracted on that day, with errors expressed at the 90% confidence interval ($n = 3$)

	Step1	Step2	Step3	Step4	Step5
	Ultrasound extraction				
Cr	0.39 \pm 0.15	42.4 \pm 5.1	24.4 \pm 5.4	11.9 \pm 3.3	20.9 \pm 5.1
Mn	57.5 \pm 4.3	17.4 \pm 3.8	8.26 \pm 2.85	4.49 \pm 1.50	12.4 \pm 3.5
Fe	1.43 \pm 0.81	26.0 \pm 8.0	25.6 \pm 8.1	0.13 \pm 0.05	46.9 \pm 10.8
Co	29.8 \pm 7.5	16.8 \pm 4.6	14.4 \pm 3.7	14.3 \pm 4.7	24.6 \pm 6.0
Ni	34.3 \pm 8.3	11.8 \pm 7.9	20.5 \pm 6.3	33.4 \pm 4.0	0.13 \pm 0.22
Cu	1.95 \pm 1.70	4.67 \pm 4.71	29.1 \pm 9.5	38.3 \pm 9.2	26.0 \pm 4.6
Zn	39.8 \pm 12.1	21.7 \pm 7.7	26.2 \pm 9.5	6.14 \pm 2.38	6.15 \pm 2.31
As	25.0 \pm 3.4	17.8 \pm 3.5	21.4 \pm 6.5	26.6 \pm 6.2	9.27 \pm 6.90
Cd	19.7 \pm 7.7	27.2 \pm 7.7	20.1 \pm 7.4	21.8 \pm 7.4	11.3 \pm 4.5
Pb	1.59 \pm 0.37	27.2 \pm 8.3	55.0 \pm 6.8	4.38 \pm 1.67	11.81 \pm 7.31
	Conventional extraction				
Cr	0.21 \pm 0.27	40.2 \pm 7.4	26.3 \pm 7.2	10.9 \pm 3.8	22.3 \pm 8.1
Mn	59.7 \pm 8.8	14.4 \pm 6.6	5.01 \pm 2.23	6.29 \pm 3.03	14.7 \pm 6.6
Fe	1.38 \pm 0.58	28.1 \pm 4.8	23.9 \pm 7.3	0.16 \pm 0.05	46.5 \pm 7.6
Co	32.9 \pm 10.1	10.8 \pm 5.2	2.40 \pm 1.72	20.9 \pm 6.3	33.0 \pm 11.9
Ni	37.9 \pm 7.8	13.6 \pm 6.5	14.1 \pm 6.6	32.3 \pm 7.5	2.10 \pm 0.58
Cu	3.20 \pm 1.82	6.80 \pm 2.16	25.8 \pm 8.2	31.1 \pm 3.5	33.1 \pm 7.1
Zn	48.5 \pm 10.5	21.7 \pm 7.2	17.4 \pm 7.2	7.70 \pm 5.45	4.70 \pm 4.62
As	26.1 \pm 4.9	11.5 \pm 5.4	18.6 \pm 5.6	34.1 \pm 10.9	9.70 \pm 3.74
Cd	18.3 \pm 8.0	20.4 \pm 7.4	30.5 \pm 7.4	20.9 \pm 8.2	9.90 \pm 3.6
Pb	1.10 \pm 0.74	15.3 \pm 3.9	61.1 \pm 11.1	17.7 \pm 9.9	4.80 \pm 1.41

the mean values obtained by the ultrasound method are comparable with those obtained by the conventional method. There were, however, a few exceptions to this agreement. For example, the ultrasound method could extract six times more Co in step 3 than the conventional extraction. The long shaking time used in the conventional method may be responsible for this difference, as it could allow the extracted element to be redistributed in the liquid–solid phases of the extraction system.

Table 4 also shows that the reproducibilities of the methods were comparable. The reproducibility was acceptable for the types of samples being analysed but, as would be expected, elements detected near the limits of detection had much greater uncertainty. The implications of the reproducibilities of the methods are discussed in the next section. The comparison of the results obtained for the compost reflected those obtained for the BCR certified reference material with the partitioning profiles being sufficiently similar such that only ultrasound extraction was applied to the remainder of the samples.

The partitioning study by ultrasound extraction in the composting process. Ten elements, Cr, Fe, Mn, Co, Ni, Cu, Zn, As, Cd and Pb, were chosen for the partitioning study. Fe and Mn are included in this study not because of their potential toxicity in the environment, but because they are known to be heavily involved in the microorganism respiration.¹⁵ To ensure the accuracy of extraction and determination, recovery experiments were also carried out. The concentrations of each selected element in steps 1–5 were summed up and compared with the nitric acid total of that sample. The overall recoveries were in a range of 87–106% for all the samples. Fig. 2 shows the partitioning results obtained with ultrasound extraction for all the elements.

In the following discussion only the major trends are discussed, as smaller variations may be reflecting the reproducibility of the data rather than actual changes. In particular, as can be seen in Table 4, the error is high in those steps where only small fractions of the element are extracted: it is, however, the overall partitioning that is important and these small fractions are insignificant. Looking more carefully at a particular set of data the trends can be clearly identified. For example, looking at Fig. 2 for chromium, very little is extracted in step 1, so although the RSD is high (Table 4) it is not important. In steps 2 and 4 significant amounts of

chromium are extracted. For step 2 on day 1, 42.4% is extracted, whereas on day 162, 6.72% is extracted; this change is significantly higher than the 5.1% uncertainty. This clearly shows a significant trend as the process continues with time as compared with the results for step 3 that would be less conclusive.

Step 1. The first step (extraction with diluted acetic acid) represents the most labile form of the elements. From Fig. 2 it can be seen that only small fractions (generally less than 5%) of Fe, Cr, Cu and Pb are extracted, whereas Mn, Zn and As are readily available (20–60%); Co, Ni and Cd fall into an intermediate group with the fractions extracted being between 5 and 30%. With the progress of composting, the availabilities of Co and Ni decrease noticeably owing to their increased complexation with organic matter, most likely the humic acid formed in the composting process. While for Mn, Zn and Cd such decreases in availability were only observed as the compost reached maturity, suggesting that their availabilities to acetic acid are strongly affected by the redox potential (E_h) of the compost system, as once the compost was deemed mature no turning was performed to supply oxygen. In contrast the availability of Cr and Fe increased once maturity was reached. Under these anaerobic conditions it is possible that more insoluble iron(III) oxide is reduced to the more soluble divalent form and serves as electron acceptor in microbial respiration.¹⁵ It is interesting to note that around 50% of Mn can be readily extracted by acetic acid, which means that half of Mn may stay in its divalent ionic form in the composting system and at the same time Mn(II) has poor sorption with humic acid.¹⁶

Step 2. The second step extracts the reducible species or those species trapped with Fe and Mn oxides. There is very little change in the percentage extracted from this step during the active composting process. Cr can be seen to be an exception as the initially high fraction (more than 40%) decreases as the composting process proceeds. This may be caused by the reduction of Cr(VI) to Cr(III) by microorganisms, followed by the combination of Cr(III) with decomposed organic materials. As would be expected for most elements in the study, their availabilities to reducing reagents decreased as the compost

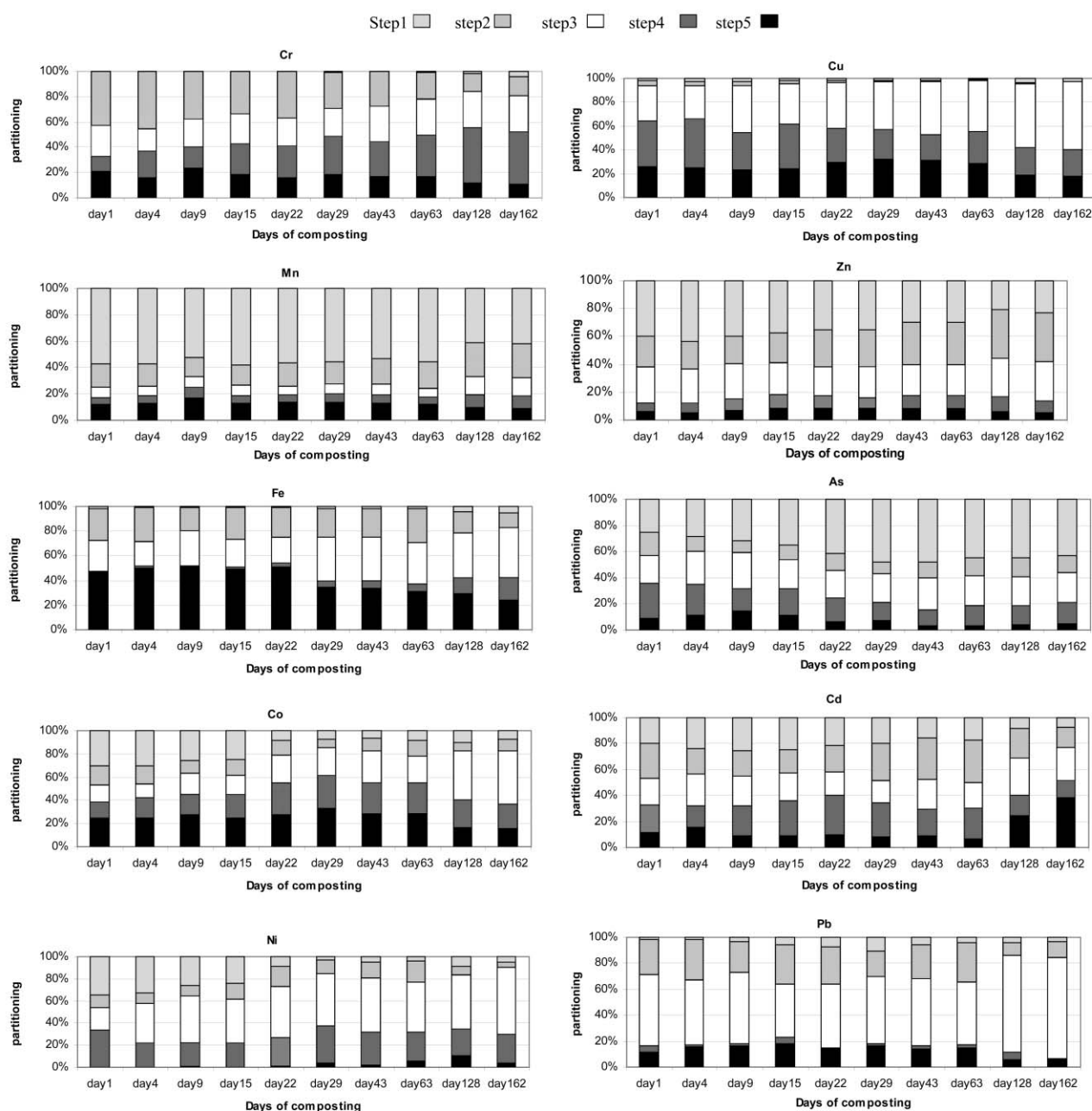


Fig. 2 Elemental partitioning profiles in composting process.

matured due to the anaerobic condition at this stage. The opposite trend was seen for Mn and Zn and the reason for this still needs further investigation.

Step 3. This step was the newly added step (extraction with 0.1 mol l^{-1} sodium pyrophosphate) which was designed to give more detailed information about the type of organic matter with which the metals were combined. From Fig. 2 it can be seen that, with the exception of Mn, most of the elements in the study are readily available for extraction in this step. A slight increase in the amount extracted in this step was seen as the composting process continued and more humic substances were formed for the metals to complex with. This phenomenon is more obvious in the cases of Fe, Ni, Cu and Pb, which are known to strongly complex with humic acid.¹⁶

Step 4. Oxidation with hydrogen peroxide simply destroys all the organic materials and releases the combined metals. As the elements extracted in step 3 were those bound with humic

substances the elements extracted in this step are those combined with organic matter other than humic acid. In the long term decomposition of organic matter you would expect the transformation of humic acids to humin, which is insoluble at all pH values. This would be seen as a decrease in extraction of elements at step 3 and an increase in step 4 but the timescale for this would be longer than the experiment. In Fig. 2 the step 4 extraction for Cr, Mn and Fe could be showing such a trend.

Step 5. The residues obtained in the last step do not usually change very much in the composting process. However, it is interesting to note that the percentage extraction for this step varies greatly for different elements. For example, Fe has a high partition of residue while another similar transition metal, Ni, has virtually no residue (less than 2%) after the four step extractions. In the case of Fe, a gentle decrease in the percentage extraction can be seen in Fig. 2, which is more marked in the mature compost. This can be explained by the micro-organism reduction of iron oxide during microbial respiration.

Conclusions

Time-consuming sequential extraction procedures have been shown to be considerably accelerated by the use of ultrasound extraction. The procedures are speeded up at the extraction steps: for example, in the standard method each extraction step takes 16 h whereas with the ultrasonic extraction method developed in this work each step took 15 min. The ultrasound emitted from the probe worked by efficiently breaking down the solid particle size, exposing fresh surfaces to be attacked by extraction reagents and causing vigorous agitation. Before carrying out the ultrasound extraction, the output power, running time and mode of sonicator, the probe and position of the probe in the solution need to be optimised according to the specific sonicator used in the experiment to ensure that sufficient ultrasonic energy gets into the extraction system.

A five step sequential extraction procedure was developed and the results obtained from ultrasound extraction were comparable to those obtained by the conventional extraction procedure. The inclusion of a step specifically to investigate the elemental interaction with humic substances gave a more detailed picture of the chemical changes during the composting process.

The compost system studied in this work reflects a more mixed waste stream than the green waste used in the previous compost investigated. This mixed waste stream resulted in higher overall levels of metals in the mature compost with some levels being higher than the upper guideline levels given by the British Composting Association for agricultural use.

With this mixed waste stream some of the raw material was already decomposed, compared with fresh green waste in the previous study. It was found in this work that the elements tend to redistribute from their initial forms to complex forms during the composting process. A definite difference in partitioning profiles was seen for most elements in the study between samples taken during the composting process and those samples taken when maturity had been reached. For most cases, the element availability to hydroxylamine hydrochloride (step 2) decreased at maturity, but Mn and Zn behaved in the opposite

way, which may imply that other mechanisms could be involved.

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