Fly ash composting to improve fertiliser value – A review

South Africa is increasingly reliant upon coal-fired power stations for electricity generation. Fly ash, a by-product of coal combustion, contains a high total content of essential plant nutrients such as phosphorus, as well as heavy metals. If the plant nutrient bio-availability in fly ash could be improved, and the toxic element content reduced, fly ash could contribute significantly as a fertiliser source in South African agriculture. In this review, we summarise up-to-date information on the soil fertility and detoxification benefits of fly ash composting, and identify information gaps in this regard. We discuss scientific studies on the potential of fly ash based composts to supply plant nutrients and to contaminate the environment. We also explore the roles of earthworms and microorganisms in improving the decomposition process, and hence the fertiliser value of fly ash composts. Although much progress has been made, further research efforts are required to optimise microbial and earthworm activity in the decomposition process, which could further enhance nutrient supply benefits and reduce toxic elements at higher fly ash incorporation rates.

Introduction

There has been a rapid expansion in population growth, urbanisation, agricultural production and industrialisation in South Africa over the past two decades. This expansion has greatly increased electricity demand, and South Africa generates more than 90% of its electricity through coal combustion.1 South Africa has vast coal deposits, mainly in the Central Basin, covering the Witbank, Highveld and Ermelo areas.2 Coal seams that are relatively thick and close to the surface (15–50 m) allow low-cost coal mining, making thermal electricity power stations a much cheaper option than hydro- and nuclear power stations in South Africa.2 Coal-fired power stations will remain the principal power generation source for South Africa in the foreseeable future as evidenced by the construction of two new coal-fired stations (the 4764 MW Medupi and 4800 MW Kusile plants).2,3 During coal combustion, fly ash – the airborne, fine, solid residue captured from exhausts through electrostatic precipitators – is obtained, and constitutes more than 70% of the solid waste.4 Fly ash is composed of oxidised, non-combustible materials which are very fine in size (0.01–1000 µm) and is generally greyish in colour.1 Most fly ash particles are spherical in shape and the average diameter is 10 µm.5 The chemical characteristics of fly ash vary widely and are influenced by coal combustion processes, age of the ash and, most importantly, coal characteristics.6,7

Coal is classified into three broad groups based on organic maturity: lignite, bituminous and anthracite coal.1 Bituminous and sub-bituminous coals constitute more than 90% of South African coal and they are characterised by higher contents of CaO (0–40%), MgO (1–10%) and SO3 (0–10%) than the higher-grade anthracite coals.1,8 These different groups of coal also yield different classes of fly ash. Class F fly ash has a low total calcium (Ca) content which ranges from 1% to 12%, and is derived mainly from bituminous and anthracite coals, whereas Class C fly ash has a Ca content as high as 30–40% and is derived from lignite and sub-bituminous coals.1,9 Class F fly ash is mostly used in the construction industry for cement making, brick making and as road bed material because of its high pozzolanic (cementing) effect.1,9 Class C fly ash has a high Ca content, which makes it a potential neutralising agent in acid mine drainage and acidic soils.8

The physico-chemical properties of fly ash are determined primarily by the type of coal burned to produce the fly ash, hence there is significant variation in fly ash quality among and even within regions of production. The general chemical composition of fly ash consists of metal oxides that occur in the order SiO2 > Al2O3 > CaO > MgO > K2O > Na2O > TiO2, as highlighted in Table 1.1 Using X-ray diffraction, Gatiari et al.11 showed that the major crystalline mineral phase in typical fly ashes are quartz (SiO2) and mullite (3Al2O3·2SiO2), with lower amounts of magnetite and maghemite, together with lime and calcite, which give fly ash its alkaline pH. The lime occurs as particles on the surface of the fly ash spheres and is thought to originate from decarbonation of dolomite or limestone impurities during coal formation.6 Fly ash also contains toxic heavy metals which originate from rock weathering into coal basins (Table 2). From an agronomic point of view, fly ash is a potential fertiliser for crop production as it contains essential elements such as phosphorus (P), potassium (K), sulphur (S), sodium (Na) and magnesium (Mg) that are potentially beneficial to crop growth. The various concentrations of plant available and easily available (water soluble) nutrients, heavy metals and metalloids in fly ash are presented in Table 2.11,13

Agricultural application of fly ash

Fly ash is an abundant waste material which has a high total concentration of essential plant nutrients, but low bioavailability of the nutrients greatly limits its direct use in agriculture.15,16 The low nutrient bioavailability is apparent with essential nutrients such as P, as highlighted in Table 2. This low bioavailability is partly a result of the low microbial activity in fly ash, which limits its mineralisation. Even when applied to the soil, fly ash has been reported to severely inhibit microbial respiration, enzyme activity and nitrogen (N) cycling processes.17,18 The inhibitory effects of fly ash when applied to soil have been mainly observed in alkaline fly ashes such as the ones in South Africa, which is mainly attributed to the high salinity, pH, boron (B) toxicity and lack of substrate carbon (C) and N.1 Schumann and Summer19 also highlighted that the major pitfalls in direct use of fly ash include low supply of major plant nutrients, nutrient deficiencies caused by unfavourable pH, slow nutrient release and fixation of other nutrients already present in the soil solution, such as P.
in the construction industry. In the USA, China and India, fly ash generation is in the range of 30–130 million t/year; for South Africa, it is more than 28 million t/year. Enormous quantities of fly ash remain unused in South Africa, and they are deposited into fly ash heaps or dams close to power stations. They are not only an eyesore, but also a public health and environmental hazard because of fly ash erosion and leachate generation, which may result in sub-soil siltation and heavy metal pollution. Information on leachate chemistry and contaminants attenuation in acid mine drainage by fly ash and its derivatives in South Africa is available from Gitari.

Much research has been carried out to demonstrate that direct application of fly ash to the soil increases the heavy metal concentration in crops and, sometimes, in soil. For example, Pandey et al.21 mixed fly ash with garden soil at various ratios (0%, 25%, 50% and 100%) and used it as a planting medium for Cajanus cajan. They observed that heavy metal (Fe, Zn, Cu, Cr, Cd) accumulation in the crop was highly responsive to increases in the fly ash application rate. Similarly, Bliskey et al.20 observed higher concentrations of all heavy metals in fly ash treatments compared to the soil alone when they evaluated the germination and subsequent heavy metal accumulation during early growth of selected cereal crops. This higher bioaccumulation of heavy metals in fly ash amended treatments has been reported by several other researchers.23 Apart from the low nutrient bioavailability, it appears that another major concern from direct application of fly ash to the soil in crop production is the potential accumulation of toxic heavy metals in crops. Direct application of fly ash to the soil has some positive effects, but these tend to be outweighed by the negative effects as summarised in Table 3.

It is generally agreed that addition of large quantities of fly ash to soils should be done with special consideration of pH and intensive monitoring of heavy metals. There is much concern about the possible loading effects of these heavy metals through continuous soil application of fly ash and the possible leaching of the metals into groundwater. These concerns limit direct utilisation and approval of fly ash as a source of plant nutrients for most edible crops. In order to address this challenge, much research has since been dedicated towards bio-remediation strategies for fly ash, such as composting.

**Problem statement**

If the plant nutrient bioavailability in fly ash could be improved, and the toxic element content reduced, or bio-absorbed, fly ash could contribute significantly as a nutrient source in South African agriculture. As a potential solution to this problem, there is interest in research to refine the fly ash composting strategies in a cost-effective and environmentally sustainable way. We summarise up-to-date information on the effects of fly ash composting and identity information gaps in regard to fly ash composting science, with the aim of guiding future research programmes for use of fly ash as a nutrient source in agriculture. We were guided by the following questions:

1. Can the bioavailability of plant nutrients from fly ash be improved significantly through refining the composting strategy?
2. Can the plant available fraction of heavy metals from fly ash be managed through refining the composting strategy?

**Improving nutrient mineralisation in fly ash based composts**

The soil nutrient improvement capacity of fly ash composts is highly variable and largely depends on the chemical characteristics of the fly ash, incorporation ratio of the fly ash and the composting technique. The variations in fly ash elemental content (total and plant available nutrients) are presented in Table 2. The most abundant primary fertiliser nutrient in fly ash is P and it is also a major limiting nutrient to crop production. Therefore, although fly ash composts supply other important plant nutrients, in this review, we focus mainly on P supply.

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**Table 1:** Typical chemical concentrations of major elements as oxides in different fly ashes as analysed using X-ray fluorescence

<table>
<thead>
<tr>
<th>Component</th>
<th>Europe</th>
<th>China</th>
<th>India</th>
<th>South Africa</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>28.5 – 59.7</td>
<td>35.6 – 57.2</td>
<td>50.2 – 59.7</td>
<td>50.1 – 67.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.5 – 33.6</td>
<td>18.8 – 55.0</td>
<td>14.0 – 32.4</td>
<td>23.4 – 27.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.6 – 21.2</td>
<td>2.3 – 19.3</td>
<td>2.7 – 14.4</td>
<td>2.7 – 4.7</td>
</tr>
<tr>
<td>CaO</td>
<td>0.5 – 28.9</td>
<td>1.1 – 7.0</td>
<td>0.6 – 2.6</td>
<td>6.4 – 8.7</td>
</tr>
<tr>
<td>MgO</td>
<td>0.6 – 3.8</td>
<td>0.7 – 4.8</td>
<td>0.1 – 2.1</td>
<td>1.9 – 2.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.1 – 1.9</td>
<td>0.6 – 1.3</td>
<td>0.5 – 1.2</td>
<td>0 – 1.3</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.4 – 4.0</td>
<td>0.8 – 0.9</td>
<td>0.8 – 4.7</td>
<td>0.5 – 0.9</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.1 – 1.7</td>
<td>1.1 – 1.5</td>
<td>0.1 – 0.6</td>
<td>0.3 – 0.89</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.5 – 2.6</td>
<td>0.2 – 0.7</td>
<td>1.0 – 2.7</td>
<td>1.3 – 1.6</td>
</tr>
<tr>
<td>MnO</td>
<td>0.03 – 0.2</td>
<td>nd</td>
<td>0.5 – 1.4</td>
<td>0.04 – 0.5</td>
</tr>
</tbody>
</table>

Sources: *Blissett and Rowson;** Gitari et al.4,10 nd, no data

**Table 2:** Typical elemental concentrations of total plant available fraction (mg/kg) and easily available fraction (%) of selected fly ash samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Total concentration (mg/kg)</th>
<th>Plant available fraction (mg/kg)</th>
<th>Easily soluble fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>553.3 – 1197.37</td>
<td>130.0 – 256.28</td>
<td>nd</td>
</tr>
<tr>
<td>K</td>
<td>0.15 – 3.58</td>
<td>nd</td>
<td>0.23 – 0.25</td>
</tr>
<tr>
<td>Ca</td>
<td>0.11 – 22.29</td>
<td>nd</td>
<td>15.64 – 24.23</td>
</tr>
<tr>
<td>Mg</td>
<td>0.04 – 7.60</td>
<td>nd</td>
<td>0.0047 – 0.0062</td>
</tr>
<tr>
<td>Na</td>
<td>0.01 – 2.039</td>
<td>nd</td>
<td>0.76 – 0.82</td>
</tr>
<tr>
<td>Al</td>
<td>0.1 – 17.39</td>
<td>nd</td>
<td>0.0005 – 0.0019</td>
</tr>
<tr>
<td>Fe</td>
<td>3000 – 61117</td>
<td>4.83 – 136.08</td>
<td>0.00049 – 0.001</td>
</tr>
<tr>
<td>Mn</td>
<td>500 – 7509</td>
<td>0.9 – 1.55</td>
<td>BDL</td>
</tr>
<tr>
<td>Zn</td>
<td>9.7 – 23.74</td>
<td>0.6 – 0.75</td>
<td>0 – 0.12</td>
</tr>
<tr>
<td>Cu</td>
<td>32 – 549</td>
<td>0.2 – 0.92</td>
<td>0.17 – 0.92</td>
</tr>
<tr>
<td>B</td>
<td>17 – 38</td>
<td>0.5 – 0.8</td>
<td>nd</td>
</tr>
<tr>
<td>As</td>
<td>1.0 – 4.0</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Cd</td>
<td>5 – 100</td>
<td>0.03 – 0.075</td>
<td>BDL</td>
</tr>
<tr>
<td>Cr</td>
<td>143.7 – 488.39</td>
<td>0.36 – 1.04</td>
<td>0.22 – 0.54</td>
</tr>
<tr>
<td>Ni</td>
<td>33.3 – 69.85</td>
<td>0.2 – 0.3</td>
<td>BDL</td>
</tr>
<tr>
<td>Pb</td>
<td>26.5 – 121.39</td>
<td>0.17 – 0.42</td>
<td>BDL</td>
</tr>
<tr>
<td>Co</td>
<td>10 – 500</td>
<td>0.05 – 0.15</td>
<td>BDL</td>
</tr>
<tr>
<td>Se</td>
<td>0.6 – 2.6</td>
<td>0.1 – 0.4</td>
<td>2.17 – 4.83</td>
</tr>
</tbody>
</table>

Sources: *Mupambwa and Minkera;** Basu et al.3;*Ram and Mastor;** Gitari et al.4,10 nd, no data; BDL, below detectable limits

Globally, the utilisation of the various classes of fly ash falls within the 0–30% range, with most developing countries, including South Africa, utilising less than 5% of the fly ash that they produce, mostly
Traditional composting of fly ash

Traditional composting, known scientifically as thermophilic composting, is probably the oldest and most widely applied method of enhancing the fertiliser value of waste materials. It can be described as:

> The accelerated degradation of organic matter by microorganisms under controlled conditions, during which the organic material undergoes a characteristic thermophilic phase (45°C–65°C), which allows sanitization of the waste by the elimination of pathogenic microorganisms.\(^{30}\)

During the thermophilic stage, high microbial activity increases respiration and C loss, resulting in a lower C:N ratio of the compost. A lower C:N ratio is one of the important determinants of a mature compost.\(^{32}\) The end product of thermophilic composting is a stabilised and well-humified compost which should have a higher fertiliser value than the constituent materials, and no pathogens. A major disadvantage of thermophilic composting is the loss of N through volatilisation of ammonia during the thermophilic stage.\(^{32}\)

Fly ash contains 0–0.2% N and 0–0.34% C, making it an inorganic by-product.\(^{6,7}\) It cannot support microbial activity and it is not possible to decompose fly ash biologically, unless a rich and balanced C and N source is added to the compost.\(^{33}\) Hence, numerous studies have been carried out to evaluate various organic substrates as additives in biological decomposition of fly ash. Fang et al.\(^{34}\) tested the decomposition characteristics of alkaline fly ash and sewage sludge mixtures (C:N ratio of 25) and reported that fly ash incorporation rate for sewage sludge composts should not exceed 35% because the decomposition index, used to evaluate compost maturity, would be significantly decreased. This decrease was attributed to the inhibitory effect of alkaline fly ash on thermophilic microorganisms during decomposition. The high pH also causes loss of essential N through ammonification and volatilisation, thus greatly reducing microbial activity. A progressive decrease in thermophilic bacterial population and diversity was also observed when municipal green waste was amended with fly ash at 0%, 25%, 50%, 75% and 100% (w/w).\(^{35}\) The amended treatments did not reach the thermophilic phase during composting, with no or little self-heating observed beyond 75% fly ash incorporation rates. A major challenge in thermophilic composting is therefore the substantial reduction of microbial activity and decomposition rate.

Microbial activity during biological decomposition produces organic acids that can solubilise minerals associated with phosphates in fly ash, resulting in increased availability of P and other essential plant nutrients.\(^{36}\) Evidence of the occurrence of phosphate-solubilising microbes (PSMs) has existed since the early 20th century and PSMs have been used as bio-fertilisers since the 1950s.\(^{37}\) Within PSMs, the phosphate-solubilising bacteria (PSB) are more effective than the phosphate-solubilising fungi, and they generally constitute 1–50% of the soil microbial population.\(^{37}\) These PSMs release low molecular weight organic acids that bind to cations attached to the mineral phosphate, thus converting the phosphate into plant available forms.\(^{38}\) Much of the research to show the benefits of PSMs has focused on solubilisation of phosphates in fly ash, with very few studies being done on sewage sludge composts.\(^{39}\)

### Table 3: Some liming and crop nutrient supply effects from direct soil application of different fly ashes under various agricultural systems

<table>
<thead>
<tr>
<th>Experimental objective, fly ash and soil characteristics</th>
<th>Experimental conditions and treatments</th>
<th>Observations</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>To evaluate the effects of soil (Ultic and Typic Haploxeralf) application of aged alkaline fly ash from two power stations on pH, salinity, available B and P growth and uptake of B and P by rye grass. Soils had a pH of 4.7 and 5.8. The fly ash was 6 months old and had a pH of 8.9.</td>
<td>Pot experiments were carried out with fly ash being incorporated at 0, 5, 20 and 50 g/kg soil. Rye grass was grown in the pots for 300 days and well watered as well as fertilised. Plant samples were harvested five times for nutrient determination.</td>
<td>Direct fly ash addition to the soil increased pH to an average of 7.03 compared to 5.25 for the control. Originally, all the fly ashes had very low plant available P and B, hence the application did not result in any significant increase in soil P and B. However, the application of fly ash did significantly increase plant P and B. This observation highlights the need to consider the effects of fly ash on toxic nutrient concentrations in plants, even when it may not have apparent effects on soil concentration. B is toxic to plants at very low concentrations.</td>
<td>Matis and Keramidas(^{29})</td>
</tr>
<tr>
<td>To determine the impact of fly ash from Western Australia on soil physical and chemical properties, heavy metals and subsequent growth of turf grass. Fly ash had a pH of 5.5 to 7.9 and the sandy soil had a pH of 4.7 (CaCl(_2)).</td>
<td>Fly ash was applied at 0, 73, 150 and 300 t/ha. It was incorporated into the soil and 7 days later turf grass (Cynodon dactylon) was planted.</td>
<td>Direct fly ash incorporation into the soil at all levels resulted in a significant increase of soil extractable P (18.5, 42.6, 46.1 and 51.2 mg/kg, respectively) but not leaf tissue P. However, a significant increase in heavy metals was also realised for Cd, Mn, Zn and Zn.</td>
<td>Pathan et al.(^{26})</td>
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<td>To clarify the differences among plant species in their response to fly ash amendment. Two types of fly ash that were used were derived from subbituminous and alkaline coal, and had a pH of 10.8 and 9.0, respectively. The potting mixture (50:50 sand/peat mixture) had a pH of 6.5.</td>
<td>The test crops were canola, radish, field peas, lucerne, barley and rye. Radish and rye grass were planted in potting mixture and the other crops were planted in soil. Ashes were applied to the pots at 0, 2.5, 5, 10 and 25 t/ha and fertiliser (8:3:8) applied at 20 days after planting.</td>
<td>Both types of fly ash significantly increased growth rates and concentrations of chlorophyll a and b at application levels of 5 t/ha, but reduced carotenoid concentrations. Addition of ash at all rates increased CO(_2) assimilation of barley and radish. Application of ashes up to 5 t/ha also increased transpiration in barley. In this study, all crops showed a general difference in response to fly ash application rates, highlighting the need for crop specific recommendations for field application of fly ash.</td>
<td>Yunusa et al.(^{27})</td>
</tr>
<tr>
<td>To investigate the impact of fly ash amendment of soil on microbial responses, extent of heavy metal accumulation in the soil and rice crop growth. Unweathered fly ash with a pH of 7.7 and soil (Inceptisol) with a pH of 5.8 (in water) were used.</td>
<td>Pot experiments were carried out using 10 kg soil mass after fly ash amendment at 0, 5, 10, 20, 40 and 100% on a volume basis. Each pot was planted with 25-day-old rice seedlings and fertiliser (20:40:20) was applied to each pot. Destructive sampling was done at panicle initiation and at harvest.</td>
<td>Significant increases in crop growth parameters (chlorophyll content, plant height, leaf area index, number of panicles) were observed at fly ash application rates of 5–20%. Beyond 20% direct fly ash incorporation, significant differences were observed in heavy metals (Fe, Mn, Zn, Cu, Pb, Cr and Cd). Application of fly ash above 40% significantly influenced the microbial population dynamics and enzyme activity. These results highlighted the potential heavy metal toxicity effects of fly ash which are likely to be greater under repeated applications.</td>
<td>Nayak et al.(^{28})</td>
</tr>
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</table>
P in rock phosphate,\textsuperscript{39,40} and limited information is available on the role of PSM strains in enhancing solubilisation of fly ash P.

It would be interesting to test the effects of special microbial cocktails such as Effective Micro-organisms (EM) on the decomposition rate in fly ash based composts. According to the Japanese inventors of the technology, EM is a mixed culture of natural and beneficial microorganisms, which form clusters to make a food chain, living in a symbiotic relationship.\textsuperscript{41,42} Effective microorganisms include predominant populations of lactic acid bacteria, yeasts, actinomycetes and photosynthetic bacteria.\textsuperscript{43} Anecdotal evidence suggests that the use of EM as an activator can bring down the traditional composting period from 12 weeks to 4 weeks.\textsuperscript{44} At present, in reference to traditional composting of coal fly ash mixed with different organic wastes, there is a paucity of information on the effects of EM on composting processes. It is necessary to determine if the groups of microorganisms within the EM cocktail are sufficiently resilient to remain active during composting of fly ash mixtures, and, if so, to identify the optimal EM inoculation level.

### Vermicomposting of fly ash

Earthworms have an important role to play in enhancing bio-degradation and stabilisation of organic wastes. Vermicomposting has been defined as a process in which earthworms interact with microorganisms and soil invertebrates within the decomposer community, strongly affecting decomposition processes, accelerating the stabilisation of organic matter, and greatly modifying its physical and biochemical properties.\textsuperscript{45} Earthworms are the crucial drivers of the process, as they mechanically fragment the waste with their gizzards and increase substrate surface area, thus altering micro-flora activity.\textsuperscript{46} Earthworms significantly increase conversion of micronutrients into plant available forms in fly ash and cow dung compost mixtures.\textsuperscript{47} However, as indicated previously, fly ash is devoid of C and N, which are essential components for any biological process, therefore, for vermicomposting, fly ash should also be enriched with a C and N source. There is theoretical evidence suggesting that microbial activity in fly ash based composts can be enhanced by adding earthworms to the composts.\textsuperscript{48,49} Earthworms modulate the microbial community and tend to selectively feed more on fungi than bacteria.\textsuperscript{50} Earthworms carry microbes in their digestive system, possibly shielding them from the direct adverse environment brought about by fly ash addition. Thus, better results at higher incorporation rates of fly ash (up to 50% to organic waste) have been reported when earthworms were added to the compost.\textsuperscript{14,44} During vermicomposting, earthworms secrete mucus which moistens the waste, and also provide a more habitable environment for waste biodegradation through their gut microorganisms. Research is, however, required to determine the interactions of various earthworm species with combinations of EM.

There are more than 3000 known species of earthworms, which can be divided into three categories based on their feeding behaviour, burrowing habit, habitat, body size, fecundity, casting activity and mobility.\textsuperscript{51} Surface feeding earthworms, known as ‘epigeic earthworms’ have an important role to play in organic waste bio-degradation and stabilisation.\textsuperscript{32,34} This group of earthworms is widely used for vermicomposting and includes Eisenia fetida, Eisenia andrei and Eudrilus eugeniae.\textsuperscript{27,34,36} Eisenia species could be the most effective organic waste decomposers during vermicomposting.\textsuperscript{26} This species is ubiquitous and resilient, and can feed on a wide range of organic materials and has good tolerance to a wide temperature and moisture range.\textsuperscript{32,44}

Cow dung appears to be one of the most commonly preferred substrates for enriching fly ash with C during vermicomposting. Several studies have evaluated the transformation of nutrients during fly ash vermicomposting using various species of earthworms, mixed at various ratios with cow dung and other waste materials. Using a non-specified earthworm species, Bhattacharjee et al.\textsuperscript{57} evaluated cow dung, soil and fly ash mixtures. The first trial period was first mixed with soil at a ratio of 2:5 and then fly ash was incorporated at six levels (5%, 10%, 15%, 25%, 40% and 50% w/w) to achieve a final weight of 700 g. These mixtures were moistened to 40–45% and then inoculated with 25 earthworms. The earthworms not only survived in the cow dung–soil mixture amended with fly ash up to 25%, but they also bio-accumulated Pb in their bodies. However, the moisture content used in this study (40–45%) may not have been the optimum for maximum activity of the earthworms, which prefer moisture contents of 50–90%.\textsuperscript{26} The pH of the cow dung–soil–fly ash mixtures was not optimised in this study, which could have affected the vermicomposting process. With an optimal moisture content and 

### Fly ash composting to improve fertiliser value

In another cow dung–fly ash vermicomposting study, Bhattacharya and Chattopadhyay\textsuperscript{46} evaluated the potential of E. fetida for improving compost plant available P levels at 25%, 50% and 75% fly ash to cow dung mixing ratios. Earthworms proved superior in increasing the phosphate-utilising bacteria responsible for conversion of P to plant available forms compared to the control with no earthworms. The fly ash incorporation ratios of 25%, 50% and 75% contributed 10.8 mg/kg, 42.8 mg/kg and 12.7 mg/kg of P, respectively, after 50 days. However, it also appears that in this study, the C:N ratio and earthworm stock density were not optimised for effective vermicomposting. It is possible that even better results could have been obtained with an optimal substrate C:N ratio and earthworm stock density. Other fly ash vermicomposting studies, e.g. Ananthakrishnasamy et al.\textsuperscript{58}, did not report plant available nutrients in the composts, but rather measured the total nutrients which are most likely to increase as a result of the concentration effect from weight loss during composting, rather than exclusively earthworm activity. Substrate C:N ratio and earthworm stock density strongly influence the vermicomposting process.\textsuperscript{26} There is also a lack of information on the types of microbes that flourish under different fly ash incorporation ratios from these studies. Such information is required as it could form a basis for development of specialised microbial cocktails for effective bio-conversion of fly ash. Recent studies at the University of Fort Hare in South Africa, using E. fetida and fly ash, cow dung and waste paper mixtures indicated that a 2:1 (cow dung–waste paper: fly ash) ratio, which gives a C:N ratio of approximately 30, may be the most appropriate, as reflected by rapid decomposition and the increase in extractable P.

Fly ash–cow dung compost mixtures may sometimes have less extractable P than cow dung alone.\textsuperscript{14} This problem is attributed to microbial community modification as evidenced by very low levels of PSB in fly ash composts.\textsuperscript{13} In India, Bhattacharya and Chattopadhyay\textsuperscript{46} composted cow dung and fly ash at various ratios (1:1, 1.3 and 3:1) for 50 days at room temperature and observed an average occurrence of PSB of 0.067×10⁸/g for the fly ash treatments compared with 1.43×10⁸/g for the cow dung alone. This microbial modification can be corrected by introducing earthworms, as shown in the follow-up study, in which the average occurrence of PSB significantly increased to 30.3×10⁸/g compared with 33×10⁸/g for cow dung alone. This finding also corresponded with the fly ash modified treatments which yielded 54.7% (79.9 mg/kg) more extractable P under vermicomposting than the same treatments without earthworms, which had 51.6 mg/kg.

### Reducing the content of toxic heavy metals in fly ash composts

#### Toxic heavy metals in fly ash

Toxic heavy metals in fly ash limit its use as a direct source of nutrients in agriculture. A high soil concentration of toxic heavy metals hinders soil microbial activity,\textsuperscript{14} thus affecting vital soil processes such as nutrient mineralisation, and effectively sterilising the soil. The plant availability of heavy metals following fly ash addition to soil tends to be variable and is controlled by the presence of Mn, Al and Fe oxides, carbonates, pH and other anions.\textsuperscript{15} For example, above pH 6, an increase in surface charge on oxides of Fe, Al and Mn, which are pH dependent, coupled with binding by organic matter, greatly lowers metal availability in soil.\textsuperscript{51} Whilst a once-off application of fly ash compost to the soil at moderate levels does not seem to present much of a heavy metal problem, the potential fly ash was first mixed with soil at a ratio of 2:5 and then fly ash was incorporated at six levels (5%, 10%, 15%, 25%, 40% and 50% w/w) to achieve a final weight of 700 g. These mixtures were moistened to 40–45% and then inoculated with 25 earthworms. The earthworms not only survived in the cow dung–soil mixture amended with fly ash up to 25%, but they also bio-accumulated Pb in their bodies. However, the moisture content used in this study (40–45%) may not have been the optimum for maximum activity of the earthworms, which prefer moisture contents of 50–90%.\textsuperscript{26} The pH of the cow dung–soil–fly ash mixtures was not optimised in this study, which could have affected the vermicomposting process. With an optimal moisture content and...
the heavy metal dynamics in soil under continuous application of fly ash composts in the current literature, and it may be necessary to establish or model the cumulative heavy metal load associated with such.

Earthworms have the capacity to bio-accumulate heavy metals, suggesting that earthworm harvests from the composts can be used to reduce the heavy metal load. The effects of vermicomposting as a possible way of reducing the heavy metal concentrations of fly ash and cow dung mixtures have been investigated. Gupta et al. started with 2 kg of feed consisting of varying proportions (20%, 40%, 60% and 80% w/w) of fly ash in cow dung with 125 mature earthworms (E. fetida). After 30 days, the earthworms and casting were separated and the reactor contents discarded, and a new set of 2 kg material added to which the earthworms from the previous 30-day period were added. A total of six runs of 30 days each were done following which various parameters were determined. Reductions of 85%, 77.2%, 68.8% and 33.5% for Cr and 78.8%, 69.4%, 83.7% and 25.3% for Pb when fly ash was incorporated at rates of 20%, 40%, 60% and 80%, respectively, were reported from this study. Gupta et al. reported that earthworms bio-accumulated on average 58.1 mg/kg Cr and 42.8 mg/kg Pb after 180 days of vermicomposting fly ash and cow dung mixtures and had an average 52.5 mg/kg Cr and 43.5 mg/kg Pb. Bhattacharya and Chattopadhyay also reported a decrease in levels of easily extractable Cr, Cd and Pb in all treatments as a result of vermicomposting after 50 days compared to the respective treatments without earthworms.

A refinement of the composting strategy will indeed improve the nutrient bioavailability and reduce the heavy metals in the large quantities of fly ash produced by coal-fired power stations. Although there is currently limited scientific information on the economics of composting, and more especially fly ash composting, the proposed technologies for fly ash composting make cheap and abundantly available waste materials such as cow dung, food waste, saw dust and waste paper. The earthworms and microbial populations do not require specialized, artificial conditions. As such, the cost associated with the composting of huge fly ash quantities should be minimal and the composting can be done at subsistence or commercial scale, enabling the production of cheaper fertiliser.

Conclusions

A comprehensive, up to date review of research on improving the fertilizer value of fly ash based composts has hitherto been unavailable. In this review, scientific studies on fly ash composting have been discussed to explore information gaps towards refining fly ash composting science. Sewage sludge, cow dung, paper and food waste are the organic substrates that are most commonly tested as sources of C and N in fly ash composting. In this case, decomposition rate, and hence nutrient release, is strongly influenced by the fly ash: organic waste mixing ratio, as well as the C:N ratio of the organic waste. The fly ash composts show great potential to supply the major elements, especially P in crop production. A major drawback to biological decomposition of fly ash appears to be the reduction of microbial activity, population and diversity. Earthworms and special microbial cocktails such as EM, PSMs and other bio-inoculants are a potential solution to this problem. Research is required to identify the microbes that tolerate high concentrations of fly ash after preprocessing, fly ash composting appears viable mostly at low incorporation rates ranging from 5% to 25%, and at these low application rates, the heavy metals emanating from fly ash composting may not be a serious challenge as they fall within permissible limits outlined for other wastes, such as sewage sludge, in South Africa. However, repeated applications of fly ash composts to the soil over time may increase the heavy metal load to toxic levels. In this regard, research efforts aimed at further reducing the heavy metal load in fly ash composts are required.

Authors’ contributions

PN.S.M. was the project leader who initiated the project under the ‘Soil Health and Sustainable Waste Management’ project and provided significant intellectual input as the team leader. H.A.M. was responsible for developing the first draft from the concepts discussed at the initiation of this review and contributed significantly during revision of the manuscript. E.D. gave significant scientific input on context and relevance and also revised and refined the manuscript to its current format.

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