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Sustainable Solutions for the Management and Valorization of Volcanic Ash

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This study proposes environmentally and economically sustainable management strategies for the valorization of volcanic ashes, addressing the significant challenges faced by cities near active volcanoes in handling large, unpredictable ashfall events. Volcanic ash collected from the 2021 eruptions of Mount Etna was characterized through physicochemical analyses, with particular emphasis on its leaching behaviour. This preliminary assessment aimed to evaluate its potential application as a component in bio-fertilizers or soil amendments. The results show that Etna's volcanic ash (i) does not pose critical risks of pollution to the soil and (ii) can release essential trace metals that could support plant health and growth. Moreover, a management protocol for volcanic ash was proposed within the framework of a sustainable circular economy. This approach aims to ensure compliance with current regulatory standards and maximise the fate of volcanic ash as a valuable multipurpose material, minimising its disposal in landfills through alternative recovery pathways.

1. Introduction

Intense volcanic ash (VA) falls can lead to multiple adverse consequences, including reduced road visibility and traffic hazards (Contrafatto, 2017), diversion of flight routes to prevent aircraft damage (Prata and Rose, 2015), damage to crops and infrastructure (Craig et al., 2016), and health risks from inhaling fine particles (Horwell and Baxter, 2006). VA fallout also places a significant burden on local authorities responsible for its prompt and safe removal (Contrafatto et al., 2020).

The challenges associated with VA deposition in regions with active volcanoes have prompted the scientific community to explore its potential as a resource. Rather than being solely regarded as an environmental and logistical burden, VA is increasingly repurposed as a substitute for raw materials across various applications, with the construction materials sector being the most extensively studied. Thanks to its mineralogy, morphology and chemical composition, VA with high pozzolanic activity can be used as supplementary cementitious material (Presa et al., 2023), while VA with low pozzolanicity can be employed as an aggregate (Contrafatto, 2017). Furthermore, based on its Si, Al, and Ca content, VA can be used in the production of geopolymers (Bernardo et al., 2022) and ceramic materials (Belfiore et al., 2020). In some cases, VA provides additional benefits, such as in brick manufacturing, where it reduces water demand (Cultrone, 2022). VA may also serve as an alternative filler material in hot-mix asphalt (Fayissa et al., 2022). However, the VA's high compositional variability complicates consistent performance, and its irregular availability poses a significant constraint for industries that require stable and predictable raw material supplies.

Other studies have explored the potential of VA as a soil improver. El-Desoky et al. (2018) conducted a field trial to evaluate the impact of VA application on soil properties and potato crop growth. Their findings revealed a significant increase in soil moisture, suggesting that VA could serve as an effective hydrophilic soil conditioner. Although mineral fertilizers typically provide higher nutrient bioavailability, the nutrient levels detected in potato

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leaves and tubers following VA application were within an acceptable range. To optimize nutrient bioavailability between conventional mineral fertilizers and VA, Zakharikhina et al. (2016) conducted agricultural trials under varying experimental conditions, testing different doses of fresh and aged VA in combination with two mineral fertilizer dosages. The results showed a potato yield increase of 37-72% compared to the baseline (mineral fertilizer without VA) after the first year of experiments. The most favourable outcomes were observed with ocherous VA, which had a richer chemical composition, and a lower rate of chemical fertilizers. The beneficial effects of VA were attributed to its role as a promoter of biogeochemical and microbiological processes in the soil, enhancing the ability of plants to assimilate nutrients. This was supported by an observed increase in starch concentration (3-5%) in potato tubers, which was attributed to the catalytic effect of a significant deposition of various trace elements from VA. De la Rosa et al. (2023) tested different wastes as soil amendments, showing that VA had high P and K content, which led to an improved plant physiological status, and its trace elements met the threshold limits for pollution. Moreover, mixtures of organic waste (green compost or wood biochar) and VA were identified as the most promising options. Additionally, VA can enhance the soil's capacity for atmospheric CO_2 capture. Fiantis et al. (2016) observed an eightfold increase in total carbon content over time in tephra, attributed to CO_2 absorption from the atmosphere through pioneer vegetation. The biogeochemical properties of weathered tephra made it susceptible to water leaching, facilitating the release of solubilised cations and anions. This process, in turn, promoted ecological succession (from algal biofilm to lichen, moss, grass mat, and, ultimately vegetation) within a four-year timeframe.

VA leachate analysis is a crucial tool for assessing the potential release of toxic elements into the environment during rainfall events following eruptive activity (Sánchez-España et al., 2023). A protocol for VA leaching with deionized water was proposed for the assessment of hazards from leachable elements (Stewart et al., 2013). However, the single water leach may be inadequate for characterising agriculturally important elements such as S (saturation effects) and F (slowly soluble complexes) and other minor elements (Cronin et al., 2014).

The present study is an initial step toward developing environmentally and economically sustainable management strategies for the valorization of VA, addressing the challenges faced by cities surrounding Mount Etna (Sicily, Italy), which must manage the sudden and massive accumulation of VA resulting from unpredictable eruptive events. A chemical characterization of VA from the Etna area was performed to assess its potential suitability as a soil fertilizer. The analysis focused on (i) compliance with threshold values for waste recovery and (ii) the presence of beneficial leachable trace elements essential for enhancing plant health and soil fertility. Additionally, a management protocol for VA was developed to ensure compliance with current regulatory standards, promote sustainable practices, and explore diverse potential applications. This integrated approach establishes a foundation for the safe and effective reuse of VA within a circular economy framework.

2. Materials and methods

A sampling campaign of VA was conducted across multiple accumulation sites within the Etna region, following the frequent eruptive events that occurred in 2021. Sampling procedures adhered to the standard protocol outlined in UNI 10802:2013. Based on the origins and characteristics of the collected deposits, the VA samples were classified into distinct categories, as described in Table 1.

Table 1: List of VA samples from different sites of Etna's territory.

Sample identification code	Sampling area	Type of VA pile
1a	Nicolosi	Mixed (street sweeping + extra-urban or private areas)
2a	Trecastagni	Mixed (street sweeping + extra-urban or private areas)
2b	Trecastagni	Mixed undercover (i.e., piles covered with plastic sheets)
2c	Trecastagni	Street sweeping (VA with finer size)
3a	Santa Venerina	Mixed (street sweeping + extra-urban or private areas)
4c	Riposto	Street sweeping (VA with finer size)
4d	Riposto	Private collection (houses and gardens, in plastic bags)

Light and heavy hydrocarbons, including polychlorinated biphenyls (PCBs), polychlorinated triphenyls (PCTs) and polycyclic aromatic hydrocarbons (PAHs) were analysed in the VA samples. Additional analyses included the determination of the Acid Neutralization Capacity (ANC) and the residue at 105 °C and 600 °C. Moreover, the concentrations of heavy metals were quantified via inductively coupled plasma mass spectrometry (ICP-MS). ~3 g of VA sample were added to a digestion solution consisting of 21 ml of 37% HCl, 7 ml of 65% HNO_3 and Milli-Q water in a 50 ml vessel. The mixture was brought to a boil and the chemical digestion lasted 2 h at 120 °C. After solid-liquid separation using filter paper, the VA samples were analysed (NexION 350X mass spectrometer). The measured concentrations of elements were then compared against the regulatory thresholds established for soil improvers (Legislative Decree 29-04-2010, No. 75).

Leaching tests were performed, according to the methodology set by the UNI EN 12457-2 norm, to assess the concentration of leachable metals and anions from the VA. The procedure involved mixing the VA material with Milli-Q water at a solid-to-liquid ratio of 1:10. Specifically, 400 mL of Milli-Q water and an appropriate amount of VA – calculated based on its dry residue content – were added to a 500 mL jar. The mixture was then agitated on a rotary mixer at 9 rpm for 24 hours. Following the mixing period, the suspension was filtered through a standard filter in a funnel and aliquots of the filtrate were extracted using a syringe and passed through a 0.45 μm filter to obtain samples for ICP-MS analysis and pH measurement. The leachate was characterized for all the parameters necessary to verify compliance with the regulatory thresholds for waste recovery, as defined in Annex 3 of the Ministerial Decree 05-02-1998 (non-hazardous waste subjected to simplified procedures of recovery). Furthermore, the concentrations of leachable metals potentially beneficial to soil fertility and plant health were quantified, including macro- and micro-nutrients.
In the second part of the study, a protocol for the sustainable management of VA was drawn up based on (i) the current regulatory framework and (ii) potential applications of VA. The protocol, illustrated through a flowchart, outlines the critical steps (checks, alternative actions, challenges and possible solutions) that guide the VA management to maximise its final destination as a multipurpose raw material.

3. Results and discussion

3.1 VA characterization

No significant concentrations of hydrocarbons, PCBs and PCTs were found in the VA. PAHs were even below the detection limit. The ANC was rather low for all the VA samples, revealing a modest capacity to neutralize acid attacks. The results on the residues at 105 °C indicated a low humidity of the samples but also a resistance to absorbing water. A correspondence between the residue values at 105 °C and 600 °C was observed, thus demonstrating the limited presence of organic material. The concentrations of heavy metals in the analysed VA samples were at least 70% lower than the regulatory limits (Legislative Decree 29-04-2010, No. 75). Therefore, the analysed VA from the Etna area was suitable for use as a soil improver. Moreover, the measured concentrations were comparable with those reported by De la Rosa et al. (2023).
The leaching test results are presented in Table 2.

Table 2: Leaching test results compared to the regulatory limits (M.D. 05-02-98, Annex 3) for waste recovery.

	Sample							
Parameter (concentrations in μg/L)	1a	2a	2b	2c	3a	4c	4d	Threshold
Ba	17	15	20	24	18	29	15	1000
Cu	14	16	56	12	8	13	6	50
As	1.20	1.77	2.02	1.38	1.31	1.40	0.99	50
Cr	1.01	0.60	0.98	0.72	0.87	0.64	0.42	50
Pb	3.17	1.10	3.21	4.87	3.15	2.53	1.16	50
Zn	96	22	1587	78	51	57	65	3000
Ni	4.95	4.03	1.95	1.60	1.79	1.05	0.91	10
V	7.14	7.20	9.04	7.73	9.56	6.92	4.99	250
Be	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	10
Se	<0.2	1.062	1.189	<0.2	<0.2	0.285	1.144	10
Cd	0.103	0.054	0.094	0.027	0.033	0.023	0.005	5
Hg	0.07	0.042	0.042	0.031	0.026	0.024	0.022	1
Nitrates	8960	5680	6610	7940	11,870	6970	4000	50,000
Fluorides	n.d.	2130	400	n.d.	810	1700	3540	1500
Sulphates	7020	10,100	7610	4740	5620	6020	11,86	250,000
Chlorides	29,310	28,550	16,240	14,950	14,170	23,200	25,26	100,000
Cyanides	<10	<10	<10	<10	<10	<10	<10	50
Asbestos	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30,000
pH	8.54	8.52	8.77	8.04	7.7	8.28	6.44	5.5< >12.0

Overall, three out of the seven samples (1a, 2c, and 3a) fully complied with the regulatory thresholds for waste recovery. The remaining four samples exhibited exceedances in only a single parameter. For three of them (2a, 4c and 4d), the most critical issue was the elevated concentration of fluorides, whereas one sample (2b) exhibited a slight exceedance of copper. These results suggest that the suitability of VA from the Etna volcano for recovery purposes is variable. Its compliance with regulatory thresholds appears to depend on factors such as the specific eruptive event from which the VA originated, whereas the collection conditions – linked to the degree of exposure to atmospheric agents – did not show a consistent or clearly defined effect. Concerning the fluoride release, note that the maximum value of concentration in the leachate (~3500 µg/L, sample 4d) is well below the values of 4000-54,000 µg/L reported for Tajogaite's VA (Las Palmas, Canary Islands) in the study by Sánchez-España et al. (2023). Moreover, we performed a VA washing with a 1:2 solid-to-water ratio and found that two additional VA samples became compliant with the regulatory limits. However, the management of the washing effluent may represent an environmental and economic criticality, potentially undermining the overall sustainability of the VA recovery. Another solution to reduce the fluoride concentration in the VA leachate may involve "active" storage, allowing prolonged exposure to atmospheric agents. Nevertheless, this practice could bring the side-effect of reducing the content of elements important for agricultural applications of VA.

Most samples exhibited slightly alkaline pH values, while sample 4d showed a mildly acidic pH (6.44), likely due to limited exposure to atmospheric agents. The COD was not measured. However, values lower than the regulatory threshold (50 mg/L) are expected.

The analysis of VA leachates was extended to elements beneficial for soil enhancement (Table 3).

Table 3: Leaching test results on elements beneficial for plant health.

	Sample						
Parameter [µg/L]	1a	2a	2b	2c	3a	4c	4d
Na	28,600	27,200	17,400	9100	15,400	23,320	24,300
K	3020	1260	3900	3010	3570	1640	2290
Ca	6580	7080	8840	10,030	11,550	9690	8970
Mg	1850	1800	2330	2980	3280	9690	2560
Al	716	277	784	845	670	852	660
Fe	354	330	677	546	486	394	311
Mn	9.99	10	16.95	13.82	12.35	10.49	8.35
Si	1496	1257	1879	2335	2342	1507	10,073
P	264	252	928	394	606	461	30

Several components were consistently released across nearly all samples, following a similar concentration trend: Na > Ca > Mg > K > Si > Al > Fe > P > Mn. However, despite this common pattern among elements, the overall composition of the leachates varied considerably among the samples, preventing the identification of a clear ranking or classification based on their elemental concentrations. Table 3 indicates that K was leached at concentrations of several milligrams per liter, while P was about one order of magnitude lower. Combined with the nitrate levels in Table 2 (~4–12 mg/L), this suggests that the VA can release essential macronutrients (N, P, K) for plant growth. More notably, the range of leached micronutrients may enhance nutrient availability and support plant health, for example by using VA in combination with fertilizers (see Introduction).

3.2 Protocol for VA management

The proposed protocol, outlined as a flowchart in Figure 1, begins with the collection and temporary storage of VA following an eruption. If a reuse pathway is identified within a verified production cycle, the VA must meet final product quality criteria, ensure sufficient availability over time, and comply with environmental and health standards. When these conditions are satisfied, reuse can proceed through agreements and authorizations involving public and private entities. Depending on local needs and feasibility (avoiding unsustainable transport), VA may be applied as a component of construction materials or as a soil fertilizer/improver.

If no verified production cycle for reuse is identified, or if the requirements are not met, the VA retains its classification as waste and must be managed in accordance with applicable legislation – specifically, Legislative Decree 152/2006 in Italy. In this case, an alternative pathway is followed, starting with the assignment of a European Waste Catalogue (EWC) code. As VA fallout primarily affects urban areas, the Municipalities act as the waste holders and are responsible for classifying the VA using the appropriate EWC code, in line with the European Directive of 18 December 2014. Then, the competent authority – typically the Region in Italy – must authorize a recovery procedure. This process enables the VA to be introduced into a production cycle at an existing or newly authorized facility, targeting the established "End of Waste" criteria (in Italy, article 184 *ter* of the Legislative Decree 152/2006 and subsequent modifications and integrations). If the VA can be directed to a facility previously authorized for recovery operations under the assigned EWC code, an internal verification via the Integrated Environmental Authorization (IEA) will confirm whether the conditions for the material's recovery exist. An alternative route is through an ordinary authorization issued by the Regional Authority for a new plant designated to apply recovery procedures on waste with that specific EWC code. This process must consider the origin and destination of the waste and requires the binding opinion of the Regional Agency for

Environmental Protection. Once authorized, the facility can proceed with the VA recovery, and the recovered material is subject to checks and analyses by the competent authorities (e.g., leaching tests to verify compliance with the limits set by the Ministerial Decree 05-02-1998, Annex 3). A third possibility is represented by the assignment of an EWC code for which the R10 recovery operation (*treatment in a terrestrial environment for the benefit of agriculture or ecology*) may be admitted. The plant may, for example, carry out a simple sifting/grilling of the VA material, to avoid possible contamination by plastics and/or unsorted waste, before reintroducing it into the environment. However, waste classified as "volcanic ash" is not mentioned for R10 in the Ministerial Decree 05-02-98 (Annex 1). Therefore, a simplified procedure cannot be applied, and the full ordinary authorization process is required. If none of the recovery procedures is possible, the VA is landfilled.

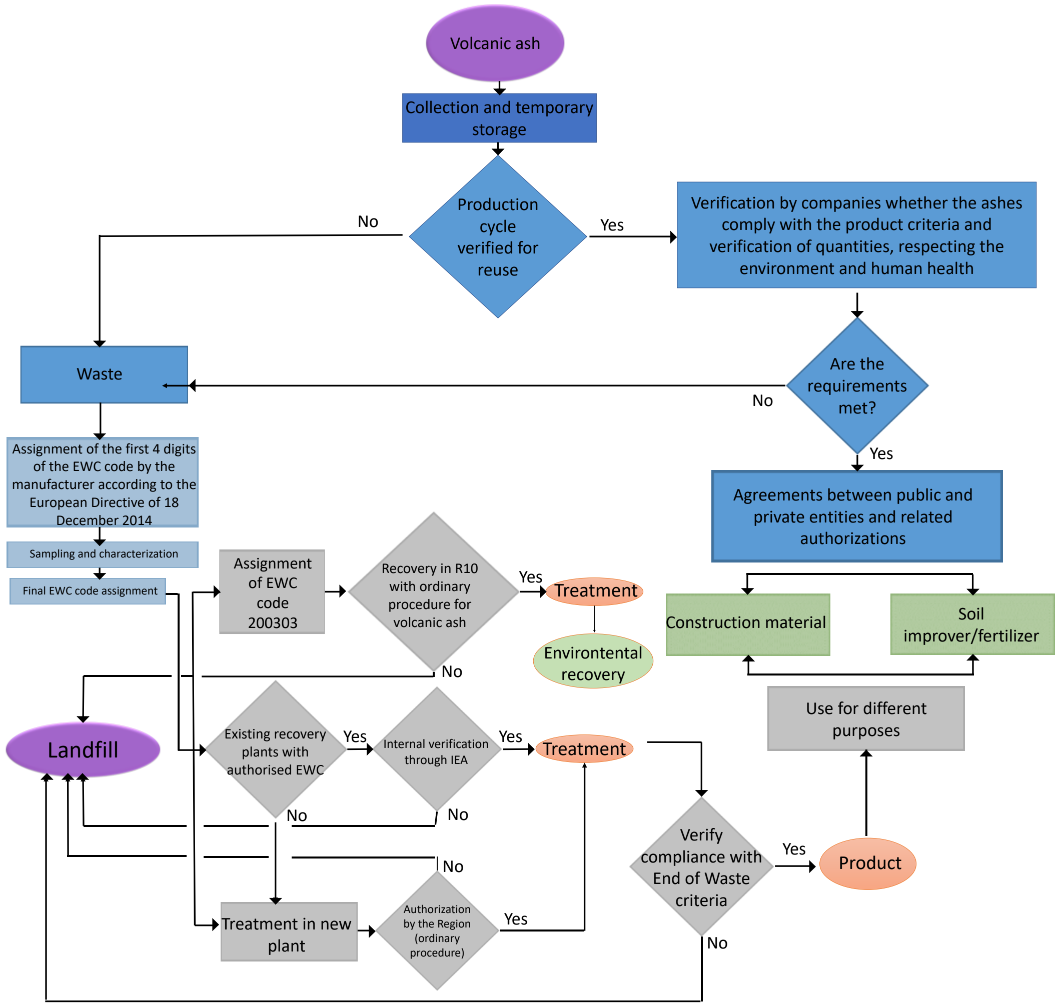

Figure 1: Protocol proposed for the management of VA in full compliance with current regulations.

4. Conclusions

This study demonstrates that the analyzed VA from Etna is a non-hazardous material with potential use as a soil improver. The physicochemical analyses showed the absence of hydrocarbon contamination and metal concentrations well below regulatory limits for soil improvers. The leaching tests showed full compliance with the regulatory thresholds for waste recovery in three of seven samples from different types of VA piles, while three others exceeded the limit for a single parameter. Fluoride release represented the main concern, but it was effectively reduced through simple washing in two cases. However, the sustainability of such treatment requires further evaluation. The analysis of VA leachates also highlighted the VA's ability to release essential elements that could enhance nutrient bioavailability. Coupling VA with conventional mineral fertilizers can improve plant growth and health, as demonstrated in the literature. However, more appealing scenarios may derive from blending VA with bio-fertilizers within a multi-waste circular economy framework. To support the effective management of VA, a protocol was developed with the objective of maximizing its use across various applications, promoting its integration into production processes in accordance with End-of-Waste criteria and regulatory compliance through multiple pathways. When strategically planned and coordinated within a holistic network of stakeholders – including municipalities, transporters, composting facilities, bio-fertilizer producers, and farmers – VA utilization could solve numerous problems caused by ashfall, ensuring timely removal from anthropized environments and promoting circular schemes.

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