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To cite this article: Dian Fiantis, Malik Nelson, Jusop Shamshuddin, Tee Boon Goh & Eric Van Ranst (2016) Initial Carbon Storage in New Tephra Layers of Mt. Talang in Sumatra as Affected by Pioneer Plants, Communications in Soil Science and Plant Analysis, 47:15, 1792-1812

To link to this article: <http://dx.doi.org/10.1080/00103624.2016.1208755>



Accepted author version posted online: 28 Jul 2016.
Published online: 28 Jul 2016.



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Initial Carbon Storage in New Tephra Layers of Mt. Talang in Sumatra as Affected by Pioneer Plants

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ABSTRACT

To date, no global data on carbon sequestration at the initial weathering phase of tephra deposits are available. To study carbon storage in the new volcanic deposit, tephra layers were reconstructed for a period of 46 months. The tephra samples were collected immediately after eruption of Mount (Mt.) Talang on 12 April 2005, over portions of the Solok District in West Sumatra, Indonesia. Pot experiments were filled with and without soil materials and covered with the collected tephra. The pot experiments were conducted in a wired house. The tephra was applied in 0, 2.5 and 5 cm depths to simulate natural tephra deposition. Every day 250 ml of filtered water was added and allowed to percolate. Solid fraction from the tephra layer was collected and analyzed at regular intervals and primary plant succession was observed over a period of 4 years. After 2 months, blue-green algae (cyanobacteria) started to colonize the bare surface tephra layer to form an algae mat. After 16 months, the surface was transformed into a green biofilm of lichen. Vascular plants (grasses and shrubs) started to be established after 2 years. Total carbon (TC) content of the tephra layer was increased significantly from 0.19 to 1.75% or eight times higher after 46 months of incubation. Higher TC storage was found in the 2.5 cm compared to that of the 5.0 cm tephra layer, which was reconstructed above the soil, with values of 1.75 and 0.89%, respectively. On the contrary, lesser amount of TC was accumulated in the single tephra layer (without soil underneath). Between 71 and 90% of TC was considered as total organic carbon (TOC). The labile organic carbon (LOC) content in the 2.5 cm and 5.0 cm of tephra layer was found to be 0.22 and 0.77%, respectively, at the end of incubation. This experiment confirmed the potential of tephra to capture carbon from the atmosphere with the help of nonvascular plants and then by vascular plants and finally sink them in the tephra layer.

ARTICLE HISTORY

Received 17 September 2015
Accepted 25 April 2016

KEYWORDS

Carbon storage;
cyanobacteria; lichens; moss;
plant succession; tephra

Introduction

Volcanic and mountainous regions are an important sink of carbon (C) among the soil ecosystem that cover from 110 to 124 million hectares, about 0.84% of the world's land surface (Kimble et al. 2000). Soils formed in volcanic deposits contain the largest accumulations of organic carbon (OC) among the mineral soil orders (Eswaran, Van Den Berg, and Reich 1993) and are estimated to be in the order of 25.4 kg m⁻² in the upper 100 cm (Batjes 1996). However, the carbon balance in this

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ecosystem can be changed markedly by natural disasters like volcanic eruptions. Volcanic eruptions are threatening events capable of producing damage to the soil surface. The area affected by the eruption of Mount (Mt.) Talang in 2005 was about 40,000 ha, with the thickness of tephra layer ranging from 1 mm to 250 mm (Fiantis et al. 2011). The volume of eruptive materials in the 2010 eruption of Mt. Merapi in Java, Indonesia, was estimated to be $150 \times 10^6 \text{ m}^3$, covering an area of about 435,000 ha (Anda and Sarwani 2012).

The Indonesian region contains 78 of the world's 550 historically active volcanoes (Simkin and Siebert 1994), ranking first in having the most volcanoes that have erupted one or more times in recorded history. The western part of Sumatra, known as the Bukit Barisan Mountain Range, is influenced by volcanic activities from several volcanoes, where volcanic eruptions have blown ash, called tephra, into the atmosphere, depositing it back on the Earth's surface. Mt. Talang is a strato volcano, formed of lava flows alternating with pyroclastic materials, emitted from various eruptive cases over the centuries. On 12 April 2005 an explosion was heard 25 km from Talang and grayish tephra ash was emitted into the sky. Tephra fell on the south and eastern-northern slopes of Mt. Talang. These new materials on the Earth's surface, consisting of abundant easily weatherable minerals, are considered important parent materials for soil formation and might also act as effective carbon sinks. Thus, the freshly deposited tephra can act as a major seedbed for primary plant succession.

Several studies have been conducted to characterize the mineralogical properties of new tephra materials (Dahlgren and Ugolini 1989; Dahlgren et al. 1999), the leaching characteristics of tephra by organic and inorganic acids (Fiantis et al. 2010a) and the prediction of the geochemical weathering indices of Mt. Talang tephra (Fiantis et al. 2010b) and Mt. Merapi (Fiantis et al. 2009), changes in the chemical and mineralogical properties of Mt. Talang volcanic ash during the initial weathering phase (Fiantis et al. 2011), and on the 2010 tephra of Mt. Merapi (Java) as a potential source of nutrients (Anda and Sarwani 2012). Tephra has numerous small particles with high specific surface areas with many reactive sites capable of absorbing inorganic and organic constituents with opposite charges (Dahlgren, Saigusa, and Ugolini 2004).

When first deposited, pristine tephra contains no OC but inorganic carbon, which originated from volatile elements ejected during volcanic eruptions as carbon dioxide (CO_2). In the absence of microorganisms during and after volcanic eruption, this CO_2 flux immediately reacts with water molecule or calcium (Ca) to form carbonic acid or calcium carbonate (Dahlgren, Saigusa, and Ugolini 2004). Tephra soon consolidates after deposition with rainfall, such as in the tropics region, to start ecosystem recovery. Microorganisms, like blue-green algae and lichens, play an important role in initiating plant succession. These microorganisms utilize solar energy to capture CO_2 with a rate of $14.6 \text{ g C m}^{-2}/\text{day}$ (Watanabe and Hall 1996) and convert the CO_2 to OC and locked it into their cell organelle (Farrelly et al. 2013).

It is well known that the secondary pioneer plants to occupy rock surface, after blue-green algae, are lichen. Chen, Blume, and Beyer (2000) reviewed that weathering of the rock surface and minerals is accelerated by lichen species. Numerous reports on lichens colonization, their physical and chemical capabilities to disrupt solid volcanic rock surface have been well documented, recently by Vingiani, Terribile, and Adamo (2013), Scarciglia et al. (2012) and Adamo and Violante (2000), on the lava flows in Canary Island (Stretch and Viles 2002), on some minerals such as hornblende (Zambell et al. 2012) and serpentine (Favero-Longo et al. 2005). However, little is known on the interface between lichen and the unconsolidated material like tephra. This plant succession and the interaction of lichen with mineral grains of Mt. Talang tephra from the initial stage were observed and reported in this study.

The accumulation of carbon by lichen was 8.02 g/m^2 in the forest soils of Norway (Vatne, Asplund, and Gauslaa 2011). The stabilization of soil organic matter (SOM) is the result of the simultaneous action of three mechanisms: chemical stabilization, biochemical stabilization and physical protection (Christensen 1996; Stevenson 1994). Carbon accumulation in the volcanic soils of Mexico increased linearly with age with a mean accumulation rate of 4.33 kg m^{-2} each 1000 years (Peña-Ramírez, Vázquez-Selem, and Siebe 2009). The accumulation of SOM due to physical

protection occurs because of the influence of aggregation and the formation of fracture planes (here referring to the sides of aggregates connected by cementing agents) that act as barriers to microbial action (Baldock and Nelson 2000; Gregorich and Janzen 2000).

Carbon pools in soils have attracted attention due to their potential as a substantial carbon sink. Carbon storage in soils tends to be concentrated in the upper mineral soil horizons and can be differentiated into inorganic and organic forms. Inorganic carbon comprises approximately a third of the total C pool in soils (Hirmas, Amrhein, and Graham 2010). Soil inorganic C consists of small fractions of C in numerous minerals, but the two most significant minerals are calcite and dolomite (Morgan et al. 2009). Several different pools of organic C in soils have been described in the literature such as labile (active C), intermediate and passive pools but not in the new tephra layer. The labile fraction of soil organic C is derived from microbial biomass and carbohydrates exhibiting relatively fast turnover rates and, therefore, may not contribute significantly to long-term C sequestration in soils. The labile organic C content in volcanic soils of New Zealand is between 3.5 and 9.0% of total organic C (Haynes 2000), and these labile C pools are the most sensitive to temperature and moisture changes (Hu et al. 1997). Nevertheless, labile soil C pools are especially important because they are easily decomposed and more vulnerable to climatic change and disturbance, and they play vital roles in short- to medium-term nutrient cycling (Silveira et al. 2008). Thus, the labile C can be used as an indicator of early changes in SOM status. The passive OC pools (sometimes called as stable or resistant humified and protected) are the more appropriate and representative fractions of sequestered C in the soil (Silveira et al. 2008). There is a close link between aggregate and soil carbon dynamics in South Chilean Andisol (Huygens et al. 2005).

Reports on the processes of organic matter accumulation and biogeochemical properties of weathered tephra and volcanic ash soils are well documented, but the short-term (<4 years) accumulation of OC is, however, not well documented. Assessment of such carbon pools is essential to reveal the potential of new tephra layers to accumulate organic matter as well as different carbon pools found on the tephra materials. The objectives of this study were: (i) to identify the primary plant succession on tephra layers; and (ii) to quantify the dynamics of carbon storage in the reconstructed tephra layer under extensive leaching conditions for over a period of 46 months. This experiment offers unique opportunities to study successive processes after ash deposition.

Materials and methods

Chemical and mineralogical characteristics of pristine tephra of Mt. Talang

Tephra used for this study was sampled immediately after deposition. Details of the study site and description of the physical, chemical and mineralogical properties of the unweathered tephra were previously published (Fiantis et al. 2010a, 2011); thus, only a summary of the important properties is provided here. The crystalline light minerals include labradorite (35%) and rock fragments (21%), whereas the heavy mineral fraction consists of hypersthene (11%), augite (3%), opaques (3%) and hornblende (traces).

The particle size of the collected material was sandy loam, characterized by coarse (2.0–0.05 mm), medium (0.05–0.002 mm) and fine (< 0.002 mm) particles with respective values of distribution of 13, 68 and 19%. Based on the silica (SiO₂) content of 57%, the tephra of Mt. Talang can be considered a basalt-andesitic ash. The alkaline earth elements such as calcium oxide (CaO) and magnesium oxide (MgO) contents found in the ash under investigation were higher than the alkali elements as potassium oxide (K₂O) and sodium oxide (Na₂O). Available phosphorus (P) in the tephra was 68 mg kg⁻¹ and the phosphate retention of tephra was about 57%. Cation exchange capacity (CEC) was low with the value of 5.50 cmol_ckg⁻¹, and the base saturation was very high, exceeding 100%. The low acid oxalate-extracted silicon (Si), aluminum (Al) and iron (Fe) of 0.07, 0.25 and 1.17%, respectively, show the scarcity of secondary short-range-order minerals present in the ash.

Incubation study

Pot-layering tephra experiments were set up in a wired house at Department of Soil Science Faculty of Agriculture Andalas University. Two series of pot experiments were run: (1) tephra layer was placed above the soil surface; and (2) a single tephra layer or without soil layers underneath. Three replicates per treatment were randomly established in a completely randomized design. The thicknesses of the tephra layer were 0, 2.5 and 5.0 cm to represent the thickness of the tephra deposit after volcanic eruption. For experiment 1 of tephra layer with underlying soils: number of samples were $27 = 3$ different thickness $\times 3$ underlying soils $\times 3$ replicates. For experiment 2 without underlying soils: number of samples were $9 = 3$ different thickness $\times 3$ replicates. Soils were collected from the A and B horizons of Andisol from Mt. Sago (160 km from Mt. Talang), Oxisol from Padang Siontah area (150 km from Mt. Talang) and Ultisol from Limau Manis area (50 km from Mt. Talang). These underlying soils did not receive any air-fall tephra of Mt. Talang. These soils were air-dried for 48 h, and crushed to pass through a 2-mm sieve. Clear or transparent polyethylene plastic pots, with diameters of 25 cm and 40 cm height, were used and filled first with soil from B horizon to a thickness of 15 cm, and then with soil of A horizon with a depth of 15 cm, followed by 0, 2.5 or 5 cm of natural pristine tephra to simulate the conditions after ash fall in the vicinity of Mt. Talang. The clear polyethylene plastic pot was used to easily observe any color changes of the tephra grains because of oxidation or reduction reaction of Fe-bearing minerals. An intravenous drip infusion set was used as rainfall simulator to apply water over the pot surface area at a height of 2 m above the pot. Every day 250 cm³ of filtered water was dripped for 1 h, allowed to infiltrate and flow out of the pots. No water was added to the pot if there was an excess of water on the surface of the tephra layer. The total volume of filtered water added during this study of 46 months was approximately 287,500 cm³, which is equal to 28,750 mm of precipitation. Every 10 cm³ of collected rainwater is equal to 1 mm. The mean annual precipitation around Mt. Talang is 2,000 mm, at Limau Manis it is around 5500 mm and at both Padang Siontah and Mt. Sago it is about 3500 mm. The water added to this leaching experiment was approximately equal to the amount of precipitation of 14 years in Mt. Talang, 5 years in Limau Manis and 8 years in both Padang Siontah and Mt. Sago.

Subsamples were taken from the tephra layer after 12, 24, 36 and 46 months to monitor tephra color, pH and OC content of the tephra layer. Morphological changes observed in the surface tephra layer were described quantitatively and photographed. Due to a devastating earthquake that hit Padang on 30 September 2009, the pot experiments were forced to be terminated after 46 months instead of the proposed 60-month period.

Methods

The colors of tephra were determined through visual comparison with Munsell Soil Color Charts. Any changes occurred on top of the tephra layer and each sidewall of the pot was photographed with a digital camera. Whenever necessary we used a ruler to measure any morphological differences in the tephra layer from time to time. The pH of the ash was determined potentiometrically in both deionized water (H₂O) and 1 M potassium chloride (KCl) with a 1:2.5 solid/solution ratio using a combined glass-calomel electrode (Tan 2005). Total carbon (TC) concentration in tephra deposit was assessed from triplicate of 0.5 g samples using a Vario EL CNS analyzer (Elementar Analysensysteme GmbH, Donaustraße 7, D-63452 Hanau-Germany). The tephra sample was ignited in a stream of oxygen at 1350°C, and the amount of carbon released was measured by an infrared detector. The Walkley and Black wet oxidation method was used to determine the total OC content (Tan 2005).

Labile OC fraction was determined by acid hydrolysis (Leavitt, Follett, and Paul 1996). The hydrolysis was carried out by reacting 1 g of air-dried tephra samples with 6 M hydrochloric acid (HCl) (ratio of 1:25) for 24 h. The residue after the hydrolysis was separated from the supernatant by centrifugation (10 min) and washed three times with de-deionized water to remove any labile OC fraction present in the tephra residue. The combined supernatant and washings were diluted to 100 ml with deionized water and analyzed for labile OC. The water-extractable OC (WEOC) was extracted with a tephra-to-water ratio of

1:5 at 100°C determined on three replicates of air-dried samples collected using the modified method of Haynes and Francis (1993). An extraction with 0.1 M sodium pyrophosphate solution (1:100) during 16 h was used to estimate OC (C_p) bonded to Al and Fe (McKeague, Brydon, and Miles 1971). Carbon was determined in 5 ml of pyrophosphate supernatant by adding 5 ml of 0.1 M potassium dichromate and 10 ml of concentrated sulfuric acid (H_2SO_4), and the mixture was left standing for 30 min. Thereafter, 85 ml of de-mineralized water was added and left to stand overnight. The C content was measured at 600 nm with a spectrophotometer (Mizota and Van Reeuwijk 1989; Van Reeuwijk 1992). Carbon content of lichen was determined by weight loss after drying at 65°C and ashing at 500°C (Tan 2005).

Scanning electron microscopy and energy-dispersive analyses (SEM-EDX) was performed at the Bio Science Institute of Universiti Putra Malaysia using LEO 1455 VP SEM attached with Oxford Inca energy 300 EDX. For SEM-EDX analysis, samples were prepared by adhering the tephra grain sample onto an Al sample holder with double-sided tape and coated with gold.

The blue-green algae, lichens and vascular plants materials were identified and authenticated by plant taxonomist at the Herbarium of Department of Biology Andalas University and Padjadjaran University Bandung. Samples of blue-green algae were collected and assessed microscopically. The species and genera were identified according to Desikachary (1959). Plant classification and nomenclature of grasses follow Backer and Van Den Brink (1968) and Gilliland (1971).

Results and discussion

Changes in color and pH

Water plays an important role in the weathering of the tephra layer. The first impact observed was transformation of tephra color. The moist color of the surface tephra layer gradually changed from light gray to very pale brown after 24 months and becoming pale brown after 46 months. The color transformation with time can be attributed to oxidation and liberation of Fe from tephra grains as well as accumulation of OC. The uppermost 1 cm of the tephra layer was observed to contain a mix of tephra grains with roots and root hairs after 46 months. The two most common pigments of the soil matrix are organic materials and Fe oxides or oxyhydroxides (Rabenhorst and Parikh 2000). Dobos, Ciolkosz, and Waltman (1990) proved that matrix soil color hue and chroma were strongly influenced by OC content, temperature and time. The chroma of matrix colors tended to decrease as soil OC increased.

As transparent plastic pots were used, any change occurring on the walls of pots was easily observed. Patches of orange color on the wall appeared after 10 days on the single tephra layer. The boundary between the tephra and soil layer turned to orange color after 20 days and from orange to reddish color after 1 month with a thickness of 0.5–2 cm. This rusty brown color is presumably due to the precipitation of Fe-bearing minerals. When we conducted EDX scan of the selected surfaces of the tephra grains, the amount of Fe was approximately between 8.58 and 12.21%. Jackson and Keller (1970) observed the occurrence of poorly crystalline Fe in thin weathering crusts beneath *Stereocaulon vulcani* colonizing recent lava flow outcrops in Hawaii as a hydrous Fe oxide with a formula close to ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$). This was most likely the noncrystalline Fe mineral of ferrihydrite.

The pH water (H_2O) of the tephra decreased from 7.26 to 4.81 for the layer with a thickness of 2.5 cm and to 4.72 for the 5.0-cm-thick layer (Table 1). The higher initial pH value for the studied unweathered tephra is believed to result in part from the rapid release of cations (e.g., calcium (Ca^{2+}) and sodium (Na^+)). All the ash samples show pH KCl values lower than pH (H_2O) and in most of the samples the magnitude of the differences is as large as 1.21–0.83.

Qualitative observation on the establishment of a vegetative layer

We witnessed the primary succession (prisere) of plant on volcanic deposits from time zero to 46 months. As the tephra layer overlying the soil material aged, the bare surface layer gradually developed into an

Table 1. Chemical characteristics of tephra before and after pot experiments.

Samples	Duration	pH (1:2.5)			Phosphate			Exchangeable Cations			CEC
		H ₂ O	KCl	Δ pH	Bray	HCl 25%	Retention	Ca	Mg	K	
untreated tephra	0 month	7.26	7.12	-0.14	68.02	4981.20	53	10.67	1.99	0.21	5.25
tephra layer of 2.5 cm	after 46 months	4.81	3.60	-1.21	18.10	3423.08	60	5.69	2.22	9.26	15.67
tephra layer of 5.0 cm	after 46 months	4.72	3.90	-0.83	10.79	3564.10	58	3.44	1.82	7.86	13.83

Samples	Duration	Oxalate extractable			Al _o + 1/2Fe _o
		Al _o	Fe _o	Si _o	
untreated tephra	0 months	0.31	0.28	0.15	0.45
tephra layer of 2.5 cm	after 46 months	0.44	0.57	0.38	0.72
tephra layer of 5 cm	after 46 months	0.37	0.47	0.25	0.60

algae surface mat after 2 months, then a lichen surface after 6 months, to a moss surface (after a further 8 months), to grass matt (after 12 months) and finally a vegetative surface tephra layer (Figure 1). However, only lichens and mosses grew on the tephra layer without soil underneath until the end of the experiment (Figure 2). The main driving force of this evolution was water. Water leached solubilized cations and anions attached to the surface of the tephra grains. After 2 months, cyanobacteria organisms started to grow, forming green thin biofilms on the 2.5 cm original bare tephra layer and 1 month later on the 5 cm tephra layer. A mix of blue algae from genus *Nostochopsis* spp and green algae of *Gloeocapsa* spp were identified in the pots as the cyanobacteria organisms. Maira, Azman and Fiantis (2006) isolated and



Figure 1. (a) Tephra was applied on the surface of soil; (b) surface of tephra layer after 4 months; (c) surface of the 2.5 cm tephra layer after 16 months and (d) surface of the 5.0 cm tephra layer after 18 months.

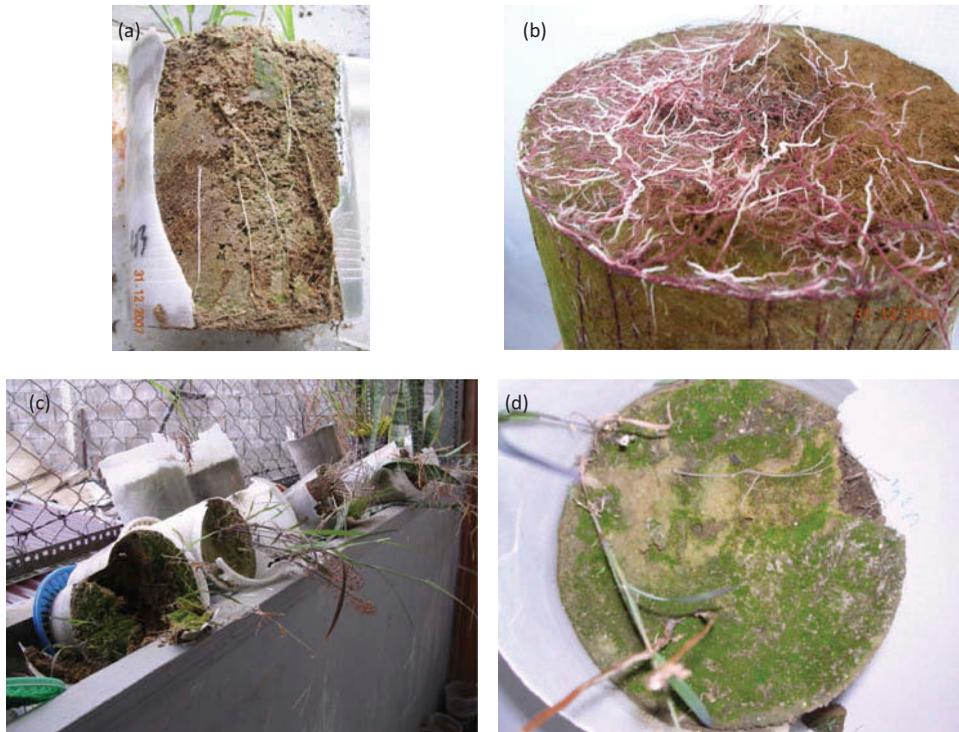


Figure 2. (a). Roots reached the bottom of the pot after 24 months; (b) the networking of white and red color of roots in the bottom surface of pot; (c) condition of the pot experiment after the 30 September 2009 earthquake; (d) broken surface of tephra after being tumbled down by the earthquake.

identified the presence of Gram negative (–) bacteria in the pore water of the tephra layer of Mt. Talang collected after 4 months.

The cyanobacteria compounds (*Nostochopsis* spp and *Gloeocapsa* spp) were the first major group of phototrophs to arise with a two-stage photosynthetic pathway capable of oxidizing water to produce molecular oxygen and able to fix atmospheric nitrogen (N) (Fay 1992). The *Nostochopsis* spp bacteria are considered as heterocyst compounds containing filaments and are truly branched (Büdel et al. 2004). The *Stereocaulon* spp are lichens-forming fungi that never developed fruiting bodies and build morphologically simple lichen thallus. *Caloplaca* spp are considered as calcicolous endolithic lichens with thallus developing inside rocks. They are primary colonizers of rock surfaces and contribute to weathering (Muggia, Grube, and Tretiach 2008). Loppi, Boscagli and De Dominicis (2004) noted that the growth and development of a cover of crustose and squamulose lichens are important for geomorphological processes and preparation of soil for the colonization by vascular plants.

By the 4th and 5th months, these cyanobacteria occupied and colonized three fourths of the upper part of the tephra layer of 2.5 cm and 5.0 cm, respectively. Then, the moss covered the whole surface of the 2.5 cm tephra layer after 6 months and after 8 months for the thicker surface. The surface of the 2.5 cm tephra layer after 8 months was transformed into a moss mat with thickness of 1–5 mm and after 10 months on the surface of the 5 cm tephra layer. After 24 months, *Caloplaca* spp and *Stereocaulon* spp appeared as dominant pioneer plants. Responses of lichens to nutrient enhancement may be considerably different, and potentially more complex, from those of vascular plants. Traditionally, it has been believed that lichens primarily rely upon atmospheric nutrient sources rather than substrate sources (St. Clair et al. 2002), although recent research has suggested this may be overstated in the case of lichen growth forms, which are closely attached to their substrate.

Vascular plants emerged on the reconstructed 2.5 and 5.0 cm of tephra layers after 12 and 16 months, respectively. They were identified as: *Hedyotis corymbosa*, *Cynodon dactylon*, *Gleichenia linearis*, *Eriochloa polystachya*, *Digitaria ciliaris*, *Cyperus anguinolentus* and *Ludwigia hyssapifolia*. Changing the pots after 2 years of study, the roots had already reached the bottom of the pot and occupied the whole bottom (Figure 3a and b). The emergence of these vascular plants, however, decreased the dominance of lichens in the colonization of the tephra surface. This is related to light limitation after extensive growing of the shrubs. The cyanobacteria, lichens and mosses were introduced by airborne seeds, while the vascular plants were originated from survival seeds and roots of underlying soil materials.

The colonization by these shrubs on the tephra layer indicates the establishment of new vegetation. Further to that, it confirmed the potential capability of tephra materials to capture carbon from the atmosphere and sink carbon in the vegetative parts of plants and in the soil as roots underneath the tephra layer. The pots tumbled down and were partly broken after an earthquake hit Padang on 30 September 2009 (Figure 2c and d). We were forced to terminate the experiments on 30 September 2009 or after 46 months; it was originally designed for a duration of 60 months.

Scanning electron microscope studies of the tephra grains after 24 and 46 months illustrated the fungal hyphae encapsulating tephra particles and physically binding them together (Figure 4). These mycobiont hyphae were identified as *Stereocaulon* spp. and *Caloplaca* spp. Comparable results were reported by Grishin and Del Moral (1996) that *Stereocaulon suvianum* grew on the friable substratum of tephra after eruptions of Mt. Kamchatka and 39 lichen species were identified in 30–100 cm depth of Mt. Kamchatka tephra layer (Grishin et al. 1996). *Stereocaulon vulcani* grew abundantly on recent lava flows on the islands of Hawaii and greatly accelerates the chemical weathering of lava's substrates (Jackson and Keller 1970). *Stereocaulon* spp are also important colonists of young volcanic sites in the Caribbean, the Azores, La Reunion, the Canary Islands and Africa (Fritz-Sheridan and Coxson 1988; Lamb 1977). Lichen accumulation on the youngest lava flows was limited most strongly by precipitation rather than by temperature (Kurina and Vitousek 1999) while the weathering of olivine and feldspars by organic acids was exuded by fungal hyphae (Jongmans et al. 1997).

New depositions of tephra are usually considered an inhospitable environment for living organisms. However, it was not the case in this study as well as observed by Burford, Kierans, and Gadd (2003) that the first species to colonize a bare solid rock or unconsolidated surface were cyanobacteria, followed by mosses. Cyanobacteria and lichens took their nutrients directly from the tephra of Mt. Talang on which they grow. Tagawa et al. (1985) observed thick carpets of blue-green algae on the new substrates of Krakatoa. They believed that these Cyanophyceae were the first plant colonizers forming the germination medium for the establishment of ferns. Grishin and Del Moral (1996) found that the first colonizers on the deep ash deposits on Kamchatka's volcanoes were members of the Jungermanniaceae (liverworts), which apparently can grow on substrates almost devoid of organic N. Mosses and algae invaded only after N levels had increased.

Contrary to the physical effect of lichens on the weathering of rocks surface by the penetration of hyphae (thallus rhizines), the hyphae in our study connected or bridged the loose grains of tephra to each other as observed by the naked eye and through SEM. Broken and etched surface condition of tephra grain was observed microscopically (Figure 5). With time, the biomass of the lichens community increased, and as the lichens died, their decomposing remains mixed with tephra materials of Mt. Talang. Lichens are composite organisms comprising a fungal component, the mycobiont, and algae or the photobiont cyanobacteria (Jackson and Keller 1970). Syers and Iskandar (1974) reviewed the various ways by which lichens are able to decompose minerals. They concluded that there were three main processes: (a) the aqueous dissolution of respiratory CO₂; (b) the excretion of oxalic acid by the growing lichen; and (c) the production of water-soluble lichen compounds, which are able to form soluble metal complexes. Thus, the accumulation of lichens biomass on the surface layer of Mt. Talang tephra provides an excellent organic nutrient base for the next subsequent heterotrophic microbiota and for mesobiota. Lichen-dominated vegetation covers

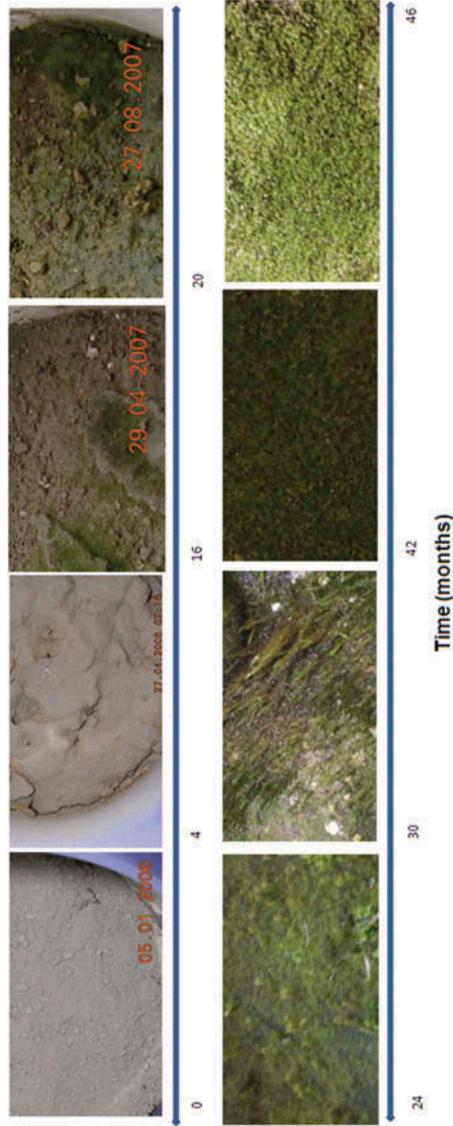


Figure 3. Primary succession observed on the 5.0 cm tephra layer of Mt. Talang incubated without soil underneath.

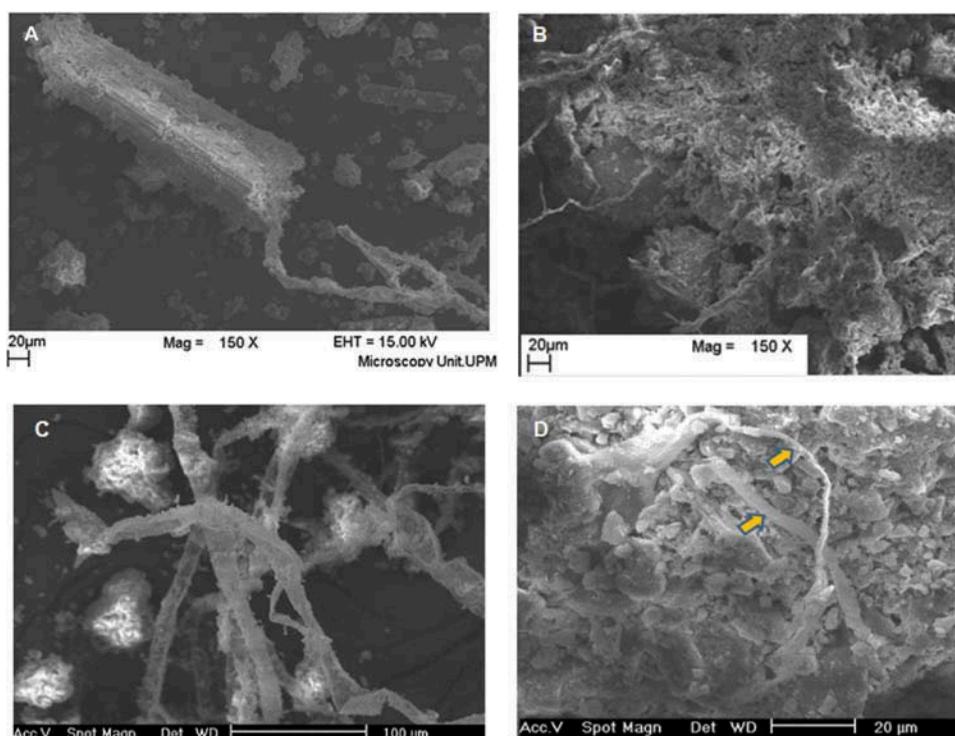


Figure 4. (A) SEM micrograph of tephra particle after 24 months attached to mycobiont hyphae; (B) Networking of mycobiont hyphae and tephra particles after 24 months; (C) SEM micrograph showing growth patterns mycobiont hyphae and physically binding tephra particles after 46 months and (D) SEM close up of tephra grain surface with fungal hyphae after 46 months.

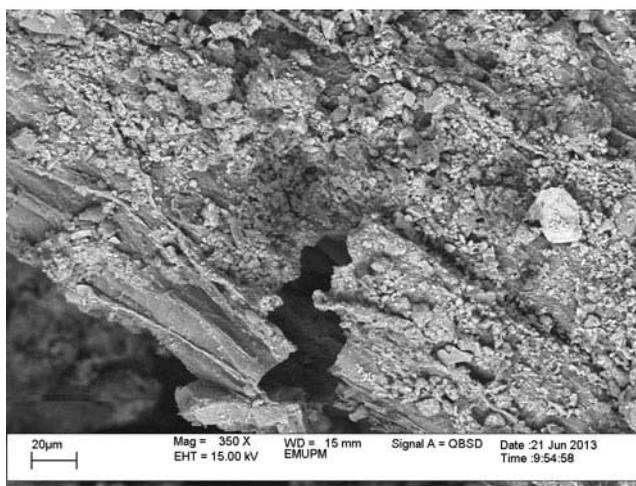


Figure 5. Broken and etched surface characteristics of tephra grains after 46 months.

approximately 8% of the Earth's surface, giving them a globally important role in plant ecology, and C, N and P cycles (Takeshi et al. 2001).

The amount of dissolved cations in pore and leached water of the tephra layer covered by lichens for 600 days was increased with time (Table 2); this proved the capability of lichens to promote

Table 2. Dissolved Ca and Mg in pore and leachate solutions.

Samples	Ca (mg/L) after (days)							
	Pore Water				Leached Water			
	30	120	240	480	30	90	240	480
Volcanic Ash (VA) 2.5 cm	34.00	25.00	9.66	6.10	308.50	277.00	3.86	2.32
Volcanic Ash (VA) 5.0 cm	65.00	55.00	30.39	17.08	344.50	376.00	11.63	6.98
Andisol + VA 0 cm	10	27.50	23.05	10.78	56	33.00	2.49	1.49
Andisol + VA 2.5 cm	256	203.00	33.64	21.95	120	185.00	43.19	25.92
Andisol + VA 5.0 cm	320	317.00	38.26	41.09	230	275.00	28.38	17.03
Oxisol + VA 0 cm	12	27.00	21.28	8.90	78	57.00	0.00	0.00
Oxisol + VA 2.5 cm	236	244.50	37.57	28.48	120	120.00	35.73	21.44
Oxisol + VA 5.0 cm	369	364.50	40.74	41.68	320	350.00	45.13	27.08
Ultisol + VA 0 cm	8	26.50	22.07	9.69	45	64.00	2.88	1.73
Ultisol + VA 2.5 cm	236	246.00	30.07	24.82	230	277.50	23.84	14.30
Ultisol + VA 5.0 cm	365	343.00	36.61	31.56	245	297.50	40.37	24.22

Samples	Mg (mg/L) after (days)							
	Pore Water				Leached Water			
	30	120	240	480	30	90	240	480
Volcanic Ash (VA) 2.5 cm	8.12	6.77	4.68	3.60	1.62	4.51	3.55	2.13
Volcanic Ash (VA) 5.0 cm	8.22	4.72	5.25	3.92	2.34	6.33	4.07	2.44
Andisol + VA 0 cm	2.23	1.98	2.62	2.82	4.39	4.08	0.19	0.11
Andisol + VA 2.5 cm	2.67	3.16	4.14	3.07	16.40	12.54	0.36	0.22
Andisol + VA 5.0 cm	4.44	7.70	4.56	3.79	19.20	17.30	0.32	0.19
Oxisol + VA 0 cm	4.63	5.29	2.71	3.17	1.34	1.59	0.09	0.06
Oxisol + VA 2.5 cm	5.47	6.35	4.94	3.62	2.88	10.04	0.42	0.25
Oxisol + VA 5.0 cm	12.4	13.56	4.83	4.01	20.43	19.84	0.42	0.25
Ultisol + VA 0 cm	1.79	3.37	1.88	2.74	1.09	1.47	0.01	0.01
Ultisol + VA 2.5 cm	3.17	4.29	4.22	3.24	3.62	5.69	0.33	0.20
Ultisol + VA 5.0 cm	4.63	5.30	5.22	3.50	8.17	8.07	0.35	0.21

biogeochemical weathering. It is believed that the biogeochemical weathering of tephra by lichens occurred through the metal-complexing action of lichen compounds. Certain lichen compounds can extract varying amounts of Al, Ca, Fe and magnesium from silicates (Iskandar and Syers 1972).

The pioneer plant evolution on the tephra layer of Mt. Talang showed great differences in the rate of vegetation reestablishment, related to the depth of the tephra blanket. Where the ash cover was shallow (2.5 cm), vegetation reestablished rather quickly, faster than on the 5.0 cm tephra layer. Lawrence and Ripple (2000) reported that revegetation was faster on thin tephra deposits after Mt. St. Helens eruption. Grishin et al. (1996) explained that revegetation by pioneer plants (lichens and mosses) on the surface of the tephra layer of Mt. Ksudach showed different stages. The first stage when lichens colonized tephra with the depth of <20 cm was in the first decade after eruption. The second stage of revegetation in tephra layer was when the thickness of tephra reached between 20 and 50 cm after 20 years; the third stage on tephra depth of 50–70 cm, predicted the plant recovery on the tephra depth 70–400 cm after 2000 years.

The presence of soil beneath the tephra layer accelerated the reestablishment of pioneer plants. No vascular plants (such as grasses or shrubs) were found on the single tephra layers with thicknesses of 2.5 and 5.0 cm after 46 months; the tephra surface was still colonized by lichens and mosses. The absence of vascular plants on the single tephra layer was due to lack of surviving seeds and roots of grasses in the experiment pot. Yet, under the SEM the surface of tephra exhibits extensive surface corrosion, deeply etched and starts to disintegrate (Figure 5), proving the capability of the hyphae of lichen to penetrate and disintegrate the mineral surface. As a result of hyphae growth and penetration, the physical weathering processes of tephra accelerate and the initial carbon storage begins.

Dynamics of carbon storage

Initially, inorganic carbon (C) was detected by scanning a selected surface of tephra with SEM-EDX with the value of 5.47% by weight (Figure 6). Then with time, OC enters the studied tephra by incorporating the blue-green algae, lichen and vascular plant materials, successively. Results showed that the total C content of cyanobacteria, lichens and vascular plants that colonized the tephra layer of Mt. Talang varied between 42.3% and 57%.

Figures 7 and 8 show the dynamics of carbon pools in the 2.5 cm and 5.0 cm tephra layers with or without soil underneath over the period of 46 months. Trends in TC accumulation in tephra layer varied depending on tephra depth and increased with time. When the tephra layer was incubated with soil materials, the accumulation of TC was significantly higher than in the single tephra layer. The amount of TC decreased as the thickness of the tephra layer increased in both experiments. At the end of the experiment, TC reached the value of 1.75% for the 2.5 cm tephra layer, but only 0.89%, 0.48% and 0.23% in the 5.0 cm tephra layer with soil, and the single tephra layer of 2.5 cm and 5.0 cm, respectively. The higher value of 1.75% of C was one-tenth of the TC content of the volcanic soils of Mt. Talang before eruption (unpublished data of Fiantis). The observed trend of increasing TC content with time implies that progressively tephra layer was capable of capturing more CO₂ from the atmosphere through pioneer vegetation. The increase of TC in the tephra layer with soil was due to more shrubs grown in pots of tephra mixed with soil. As the total oxidized OC content of pristine tephra was 0.14%, the inorganic carbon content was 0.05%.

In this study, it was found OC accumulated approximately linearly with time. A higher value was obtained in the 2.5 cm tephra layer compared to the 5.0 cm layer. The OC content of tephra layer increased significantly after 8 months and was nine times higher after 46 months as more vegetation emerged. The OC reached the value of 0.28–1.22% at the end of the incubation period, i.e., increased between 6.1 and 8.7 times in tephra deposited above the soil materials, but only 2.0–2.6 times in the single tephra layer. The amount of OC content increased as the depth of tephra layer decreased. The most probable sources of OC accumulated in the tephra layer during the first year was believed to be from cyanobacteria, the second year was from cyanobacteria and lichens, and the third to fourth year was from shrubs or grasses.

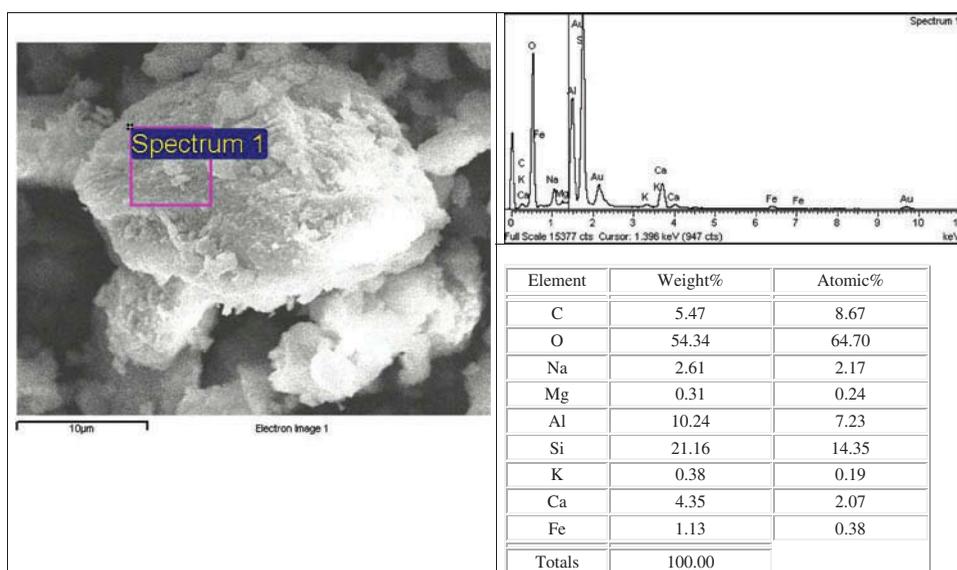


Figure 6. Surface characteristics and elemental composition of tephra after 46 months.

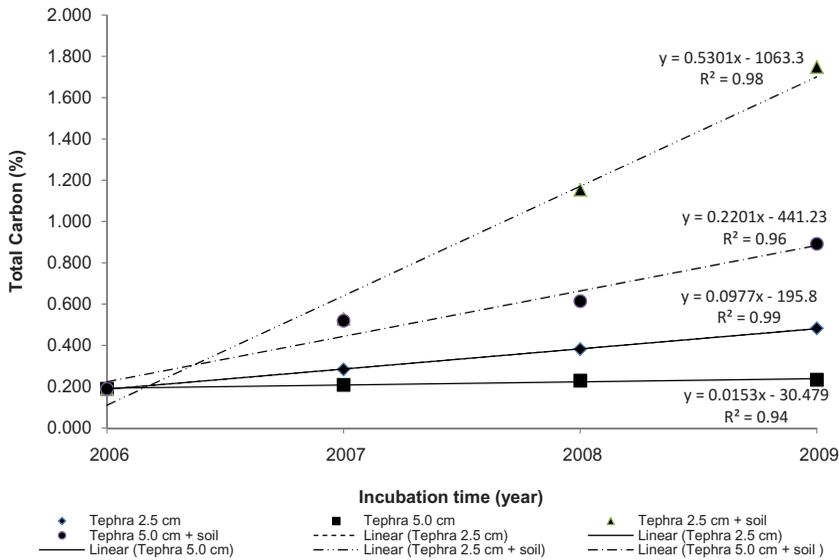


Figure 7. Changes in organic carbon and labile organic carbon content in the tephra.

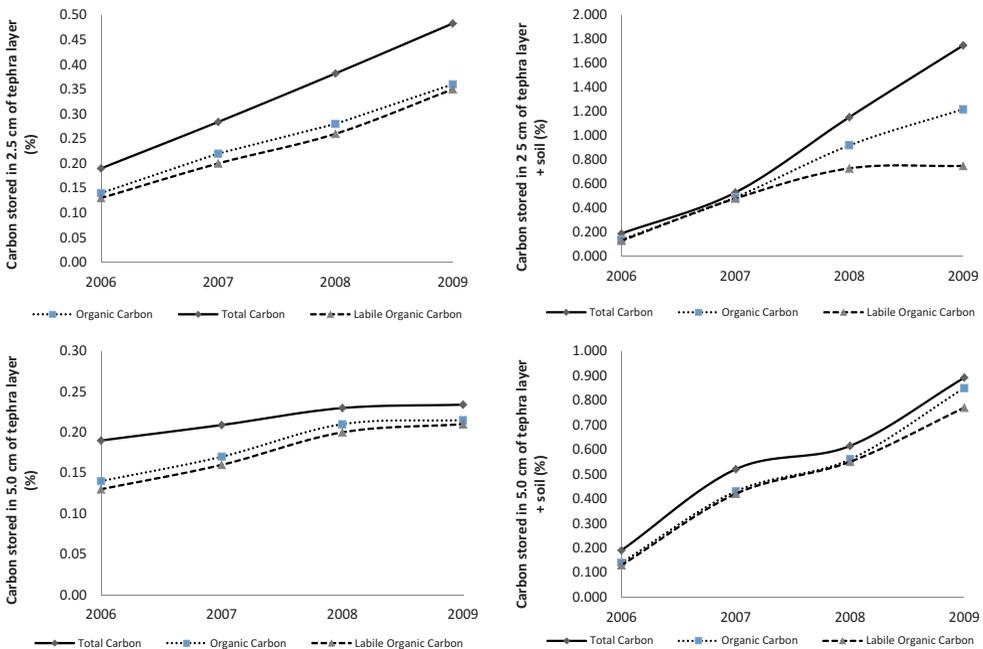


Figure 8. Dynamic of carbon storage in the tephra for 46 months period.

Cyanobacteria have the ability to utilize both CO₂ and bicarbonate (HCO₃) as an inorganic carbon source to produce biomass. Markou and Georgakakis (2011) reported that biomass concentration of *Nostoc* spp is 0.2–0.3 g/L, with the carbohydrates content ranging from 30.66 to 32.85%. Cyanobacteria take up inorganic carbon from the atmosphere and transform the inorganic carbon to OC and accumulate it in the intracellular cell with the concentration up to 500–1000-fold (Colman 1989). Addition of OC to soils by the growth of blue-green algae (*Nostoc muscorum*) or bryophyte

(*Barbularia curvirostra*) on the soil surface significantly increases soil C up to 20.9% and 23.0%, respectively (Rao and Burns 1990). Total amount of C translocated to the soils by grasses during one vegetation period is approximately 1500 kg C ha⁻¹ (Kuzakov and DoManski 2000).

Carbon content in the tephra layer of Mt. St. Helens in the cold-temperate region increased from 0 to 0.2 mg g⁻¹ after 4 years (Halvorson and Smith 2009), while the accumulation rate of OC at the surface horizon of volcanic soils originated from the tephra of Mt. Krakatau in the hot humid tropics is 45–127 g/m²/yr, reaching a value between 8.2 and 20% after 110 years of soil development (Schlesinger et al. 1998). The rate of C accumulation in the 91-year-old tephra deposit of Mt. Bandai (Japan) in the cool-temperate and humid climate is between 0.10 and 0.58 t ha⁻¹ per year, with a rapid increase of organic matter during the early stage of soil development (Morisada, Imaya, and Ono 2002). Mean residence time (MRT) of C in the volcanic soils of Ecuador ranged from 24 to 56 years (Paul et al. 2008). The MRT of each soil C pool according to Parton et al. (1987) is a metabolic pool (0.1–1 year), a plant structural pool (1–5 years), an active pool (1–5 years), a slow pool (20–40 years) and a passive pool (200–1500 years).

The concentration of OC in the surface layers of tephra implies the capacity of tephra to accumulate C and support plant succession. Transferring of carbon from the atmosphere to tephra surface in fact starts when CO₂ in the atmosphere is assimilated to OC in plant biomass by photosynthesis. Dead plant biomass is then decomposed by soil fauna and microbes, and parts of the biomass carbon are incorporated into SOC. The amount of accumulated SOC is, therefore, a function of inputs and decomposability of biomass, which in turn is determined by environmental factors and agricultural cultivation practices. The high carbon content of soils derived from tephra is due primarily to complexation with Al and Fe (Nanzyo, Dahlgren, and Shoji 1993; Parfitt, Parshotam, and Salt 2002).

Average labile carbon was higher in the 5.0 cm tephra layer deposited above soil material (0.77%) and in the 2.5 cm tephra layer with soil (0.75%), about two times greater than in the single tephra layer with a depth of 2.5 cm (0.35%), and more than three times that in the 5.0 cm tephra layer (0.22%). A similar trend between OC and labile OC content was observed in the single tephra layer during the experiment. The amount of labile OC in the first year of incubation was slightly smaller than the OC, but after the second and third years, the margin is gradually wider in the tephra layer incubated with soil, due to the emergence of lichens and establishment of grasses. Buurman, Peterse and Martin (2007) demonstrated the importance of fungal activity both by strong degradation of lignin and by the relative abundance of chitin in Costa Rican volcanic ash soils.

The labile C substrates are derived mainly from root exudation (Jones, Nguyen, and Finlay 2009; Nguyen 2009) and root and mycorrhizal hyphal turnover (Gill and Jackson 2000; Wallander 2006) and consists of simple acids, sugars and proteins. The labile OC or biodegradable compounds were preferentially removed by acid hydrolysis with maintenance of a fraction of recalcitrant bio macro-molecules (Helfrich et al. 2007). The turnover is relatively rapid being less than 5 years (Hoyle and Murphy 2006) and has been suggested as an early and sensitive indicator of SOM (Wang and Wang 2011).

The amount of WEOC was slightly increased in the second (1.1 times) and third (1.2–1.4 times) years, implying that cyanobacteria and lichens residue present during this period was not contributing significantly to the accumulation of WEOC. The increase in the amount of WEOC was more significant in the fourth year (1.70 times), suggesting the stimulating effect of grass residue to increase the WEOC pool in the tephra layer. There was more WEOC in the single tephra layer of 2.5 cm than in the other layers. The amount of WEOC was only 0.16–0.93% of the total OC and this is considered very low. The pattern of WEOC release with time was similar for both single tephra layer and combined tephra with soil layer. Data of WEOC in tephra deposit are limited in the literature as such comparison was only made with the data of WEOC in soils that are easily accessible. The amount of WEOC is in the range of 54.9–917 mg C kg⁻¹ soil in volcanic soils from Japan (Nishiyama et al. 2001) and from 0.2 to 949 mg C kg⁻¹ soil in both agricultural and forest

soils (Boyer and Groffman 1996). The WEOC of agricultural soils after 50 years of cropping comprises about 2–3% of the total OC (McGill et al. 1986)

The WEOC is considered a labile fraction of OC and accounts for only a small proportion of the total organic matter in the soil (McGill et al. 1986) and is composed of organic acids, microbial biomass, root exudates and lysates (Antweiler and Drever 1983, Curtin et al. 2006) and degrades rapidly (Jandl and Sollins 1997), but plays an important or critical role in nutrient transformation in soil (Chen and Xu 2005). The WEOC contents in the soils were strongly correlated with CO₂ evolution, which would indicate that a proportion of the WEOC must be easily available for microbial utilization (Ghani, Dexter, and Perrott 2003). There are many factors affecting the quality and quantity of WEOC in soil. Besides soil water content, temperature, wet/dry or freeze/thaw cycles land use and management (e.g., fertilization and liming) can influence soil WEOC tremendously (Chow et al. 2006).

After 46 months, the average levels of pyrophosphate OC (C_p) content in the aging tephra increased in the order of 5.0 cm tephra layer + soil > 2.5 cm tephra layer + soil > tephra 5.0 cm > tephra 2.5 cm (Figure 9). Presumably, the C_p was not immediately leached away from the experimental column and retained by Al, Fe and/or Si present in the pore water as the concentrations of dissolved Al, Fe and Si in the pore water were increased with time (data not shown). The pyrophosphate OC was increased from four to nine times higher than that of the pristine condition with the value between 0.0017 and 0.0037 at the end of the incubation period.

The C_p concentrations found in this tephra deposit were much lower than those from the volcanic soils of Montane region, Ecuador (Jansen, Tonneijck, and Verstraten 2011), northwest Ecuador (Paul et al. 2008), and Azores island, Portugal (Nierop et al. 2006) and Andinopatagonian Argentina (Broquen et al. 2005). Time was the main factor of the lower value of the C_p found in the studied tephra layer. Accumulation and stabilization of C_p in the tephra layer were increased with time and the carbon was retained by either Al and/or Fe, which released from the weathering of tephra. Nanzyo, Dahlgren, and Shoji (1993) and Kögel-Knabner et al. (2008) indicated important gain and stabilization of carbon by active Al and Fe to form metal-humus complexes, which will slow down organic matter decay and cause buildup of carbon pools in volcanic ash-derived soils.

The sodium (Na)-pyrophosphate ($Na_4P_2O_7$) treatment was used to estimate the fraction of Al complexed by OM (Nanzyo, Dahlgren, and Shoji 1993). $Na_4P_2O_7$ is supposed to break down the cation bridges between exchangeable cations and OM and form complexes with polyvalent cations present at the mineral surfaces (Schnitzer and Schuppli 1989). Contributions of SOC extracted by Na-pyrophosphate have been found to vary considerably (16–100% of the total SOC), with the highest values reported from sesquioxide-rich subsoils (Parfitt, Yuan, and Theng 1999; Siregar et al. 2005; Verde, Arbestain, and Macias 2005).

Organic matter extracted from soil with alkaline Na-pyrophosphate (pH 9–10) is supposed to be liberated from metal organic associations and from mineral surfaces via desorption (Kögel-Knabner et al. 2008). Arbestain et al. (2003) reported that rhizosphere volcanic soils of Spain have the molar ratio between Al_p and C_p ranging between 0.1 and 0.9. Meanwhile, in the surface horizon of Japanese volcanic ash soil, the C_p was on average 41% ± 9% of TOC, but in the subsurface horizons the average C_p was higher 55% ± 9%. Furthermore, a substantial percentage of C was present in complexes with Al and Fe and this percentage was higher in the subsoil (Morisada, Imaya, and Ono 2002). Fe oxides are the dominant carrier for mineral-bound OM in the subsoil (Kögel-Knabner et al. 2008).

Initially, pristine tephra has a higher concentration of WEOC than C_p ; this trend continued until the end of the experiment for the single 2.5 cm tephra layer, and after 24 months, the C_p contents were higher than WEOC for the single 5.0 cm tephra layer. The increase in the C_p of both thicknesses of combined tephra and soil layers was observed after 12 months and it rapidly surpassed the WEOC after 36 months. This trend could be explained by the incorporation of new additional organic matter from the remaining lichens and grasses that grew on the tephra layer as discussed earlier. Accumulation and stabilization of C_p during 1–10 years of soil formation were the result of

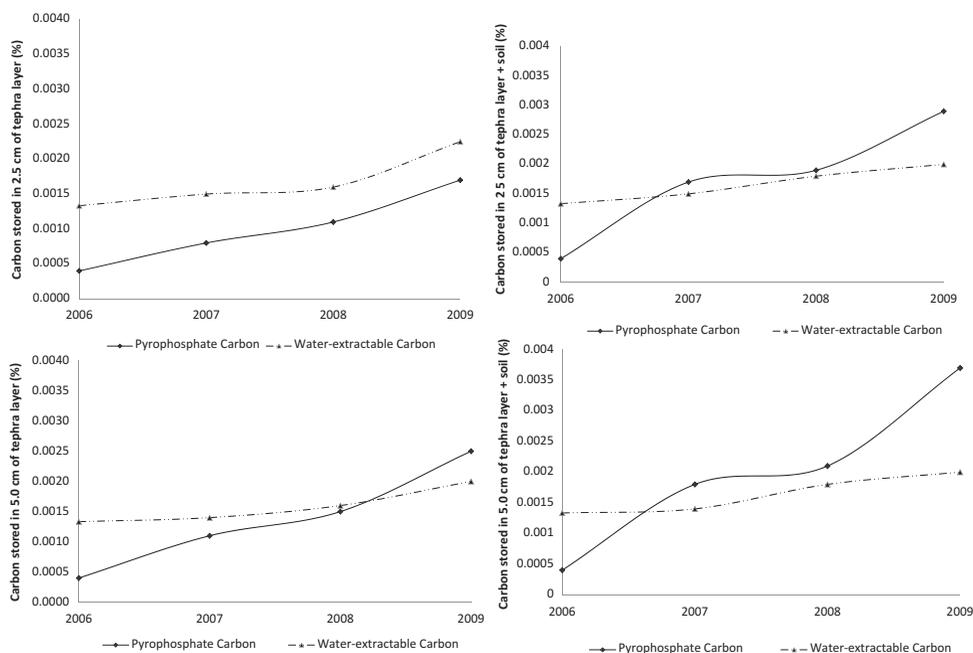


Figure 9. Accumulation of pyrophosphate carbon and water-extractable carbon for 46 months.

selective preservation of plant litter and rhizodeposits and microbial products (von Lützw et al. 2006, 2007, 2008).

Recalcitrant organic carbon (ROC) is equivalent to the difference between the TOC and the LOC; it comprises most of the slowly decomposing SOM group. Recalcitrant OC pools were very small in the single tephra layer until the end of the experiment, but not the same for the tephra layer incubated with soil. The ROC started to accumulate more after 2 years and showed an increasing trend at the end of the experiment. Recalcitrant OC in the soils consists of aliphatic plant components like lipids derived from cutans or suberans in plants and considered to be resistant to microbial and enzymatic breakdown (Baldock et al. 1997; Stimler, Xing, and Chefetz 2006).

Dissolved humic substances are assumed to be recalcitrant biopolymers, representing at least 10% of the total DOC pool (von Lützw et al. 2008). The SOC stabilization occurred via the formation of metal–humus–clay complexes and physical protection of SOC in soil aggregates (von Lützw et al. 2006) and a large accumulation of aliphatic components (Nierop and Jansen 2009). The recalcitrance of the SOC did not appear to influence SOC stabilization (Huygens et al. 2005).

Conclusion

This study demonstrated the high capability of tephra deposit of Mt. Talang to store organic matter via primary plant succession and new soil formation commencing after tephra deposition. The matrix of tephra color changes gradually with time from light gray to very pale brown and then to pale brown, which approaches the color of the soil matrix. This color transformation was due to oxidation process, liberation of Fe and accumulation of OC. The estimated TOC stored in the tephra layer was significantly increased after 4 years. The OC pools in the tephra layer consisted of total oxidized C, labile OC, WEOC, pyrophosphate OC and recalcitrant OC. Almost half of the OC stock in the upper 5 cm of the tephra layer was located in the first cm. The observed trend of increasing

carbon pools with time implies that progressively the tephra layer was capable of capturing more CO₂ from the atmosphere through pioneer vegetation. The amount of TC stored in the tephra layer at the end of the studied period was approximately one-tenth of those found in the volcanic soils of Mt. Talang, indicating progressive weathering of tephra deposits to rejuvenate soils.

Acknowledgments

We extend our thanks to Mrs. Hj. Iin Supartinah Noer of Pajajaran University (Unpad) Bandung Indonesia for her assistance in identifying the algae and lichens. The authors thank two anonymous reviewers for their constructive criticisms, comments, suggestions and editing in helping improve the manuscript.

Funding

The support of the Ministry of Research, Technology and Higher Education of the Republic Indonesia (PUPT Grant no: 37/UN.16/UPT/LPPM/2015) to the first and second authors is gratefully acknowledged.

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