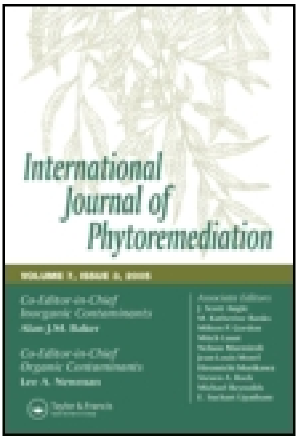

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Manab Das [a] , Palak Agarwal [a] , Reena Singh [a] & Alok Adholeya [a]
[a] The Energy and Resources Institute, India Habitat Centre, Darbari Seth Block, New Delhi, India
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A STUDY OF ABANDONED ASH PONDS RECLAIMED THROUGH GREEN COVER DEVELOPMENT

Manab Das, Palak Agarwal, Reena Singh, and Alok Adholeya
The Energy and Resources Institute, India Habitat Centre, Darbari Seth Block, New Delhi, India

Green capping is one of the popular methods to re-vegetate abandoned ash ponds of coal based thermal power plants thereby lowering the risk of contamination to the surrounding environment. It has innumerable advantages such as prevention of dust emission, checking soil erosion, stabilizing the surface areas of ash, preventing potential ground water contamination, and finally, adding native vegetation cover, which is very vital in the long term. During the early nineties and later, various reclamation projects were carried out on fly ash dumps, but until date, there have not been any initiatives to assess the alterations in physicochemical and biological properties of fly ash resulting from implementation of these reclamation projects. In the present study, three abandoned ash ponds, located in India, that were reclaimed during 1998–2003 are investigated. Marked alterations in nutritional status, microbial population, and microbial activities have been observed in reclaimed ash ponds.

KEY WORDS: fly ash, phenolics, microbial activity

INTRODUCTION

When bituminous, sub-bituminous, anthracite, and lignite coal are combusted in the furnaces of thermal power plants, they produce a range of Coal Combustion Residues (CCRs) (Haynes 2009). Based on particle size and the location of collection, CCR is categorized as bottom ash (collected below the furnace bottom), coarse ash (collected below the economizer and pre heater), and fly ash (collected below the electrostatic precipitator). The fly ash and bottom ash are generally disposed of in artificial dams, lagoons, or settling ponds, either in the form of slurry (wet disposal method), or in a dry state (dry disposal). Employing either method, ash is ultimately stored in open land (Jala and Goyal 2006), and in the due course of time become the source of fine air-borne particles that cause the deterioration of air quality of the surrounding areas. Increasing amount of CCRs generation and stringent environmental regulations continuously increase the cost of disposal, and hence various applications have been identified for utilization of fly ash: cement, concrete, bricks, substitutes for wood, components of geopolymers, synthesis of zeolite, resin and paint, mine void filling, road and embankment construction, waste land reclamation, and as amendments in agriculture (Haynes 2009). Despite such a wide range of applications,

Address correspondence to Alok Adholeya, The Energy and Resources Institute, India Habitat Centre, Darbari Seth Block, New Delhi 110003, India. E-mail: aloka@teri.res.in

at least 70% of total generation remains unutilized in lagoons and landfills. Huge volumes of fly ash (FA) that remain unutilized in dumpsites can be utilized in the establishment of vegetation and in raising forests. Green cover development over dry and barren ash ponds have various advantages: apart from creating an aesthetically pleasing landscape, it can reduce wind and water erosion, reduce leachate generation (through water loss as evapotranspiration by plants), and provide shelters for wild flora and fauna (Jala and Goyal 2006).

The typical physicochemical properties of fly ash such as their high pH-level, high soluble salt content, a phytotoxic level of B, and their lack of macronutrients, often results in the failure of plant establishment on ash ponds (Haynes 2009). On the other hand, some important attributes like high water holding capacity, availability of micronutrients, and liming capacity make it favourable for applications in agriculture (Aitken, Campbell, and Bell 1984; Yunusa *et al.* 2006). If all these attributes are addressed appropriately, ash dumps can be readily re-vegetated; the use of certain amendment like soil, compost, and or organic manure proves to be very effective in such cases (Cheung *et al.* 2000; Rai *et al.* 2004; Tripathi *et al.* 2004).

Using a cover of top soil over the ash surface is the most common method of amendment, as it provides the physical conditions and nutrient supply required for plant growth, and reduces other toxic effects of ash (Hodgson and Townsend 1973). Instead of soil, dehydrated bio-solid and composted animal or green manure are often mixed with ash to formulate a growth-supportive layer for plants. Such a mixed layer contains organic matter, which is required for nutrient cycling, supports the plant in overcoming existing physical and chemical limitations, and also encourages the establishment of self-subsistent microbial communities and increases their activities. Sometimes, the introduction of additional heterotrophic micro-flora, nitrogen-fixing bacteria, and mycorrhizal fungi are recommended to boost up the plant growth and make it sustain (Muzenberger *et al.* 1995; Gupta *et al.* 2002; Sinha and Gupta 2005).

Application of soil or organic residues adds some cost to technology but assures plant establishment (Jusaitis and Pillman 1997; Ussiri and Lal 2005). Success of reclamation of abandoned ash ponds also significantly depends on the plant species selected for the vegetation cover. Plant-species that are salt tolerant, dust and drought tolerant, and those that can grow in marginal nutrient conditions are recommended. Use of grasses like vetiver has also been found to be very effective in binding loose ash particles, and reducing wind and water erosion. A suitable combination of woody and herbaceous plant species can convert a barren ash pond to an aesthetically pleasing landscape with a new habitat of local flora and fauna (Rai *et al.* 2004; Gupta and Sinha 2008; Maiti and Jaiswal 2008). Generally, once we get an indication of the establishment of plant cover on fly ash, it is assumed that under the nurture of nature, the process of reclamation will continue in a beneficial direction. Till date, no initiatives have been taken to investigate the effects of such reclamation in long-term projects on fly ash ponds. The aim of the study is to assess and evaluate the effects of long-term bio-reclamation projects on fly ash dumps.

METHODOLOGY

Study Sites

Three study sites were chosen from three different states in India: Delhi, Chhattisgarh, and Andhra Pradesh. All these sites were reclaimed by The Energy and Resources Institute

(TERI), using selected plant species and via the application of Mycorrhizal bio-fertilizers. The indigenous mycorrhizal fungi (*Glomus* spp.) were isolated from each fly ash pond, mass multiplied at TERI and then applied at the rate of 200 infectious propagules (IP) per plant along with farm yard manure (TERI 1999).

Details of location, area covered, amendment and plant species used are presented in Table 1.

Sample Collection and Analysis

In total, 20 random ash samples (0–30 cm) were collected from each site using standard coning and quartering methods during 2010. After sieving through a 2 mm sieve, a portion of the sample was used for determining microbial biomass, dehydrogenase activity, and total phenolics; and the other portion was air-dried for analysis of physicochemical properties. The microbial biomass of the sample was extracted in a vacuum using chloroform fumigation (Beck *et al.* 1997) and the readily oxidizable carbon in the extract was determined by back titration method. From the difference of the carbon content between fumigated and non-fumigated sample, the total microbial biomass of the ash sample was calculated (Singh, Chhonkar, and Dwivedi 2007). Dehydrogenase activity was determined colourimetrically by extracting pink coloured Tri–Phenyl Formazan (TPF) (formed by the action of dehydrogenase present in sample on 2.3.5-triphenyl tetrazolium chloride (TTC) by acetone at 546 nm (Alef 1995)). Total phenolic in the ash sample was determined colourimetrically using modified Prussian blue assay method at 700 nm (Graham 1992). Gallic acid solution in methanol: water (80:20, v/v) was used for preparation of standard curve and phenolic content was expressed in terms of gallic acid equivalent (Pourmorad, Hosseinimehr, and Shahabimajd 2006). The pH was determined from a 1: 2.5 (w/v) solution of sample in water and the same was used for determining its electrical conductivity (EC). Organic carbon (OC) was determined using di-chromate oxidation method (Walkley and Black 1934). An air-dried sample was processed (along with the addition of 40% NaOH and distillation) using a KEL PLUS Nitrogen estimation system (Classic DX, Pelican Equipments) followed by determination of available nitrogen by titration with 0.02 N H_2SO_4 (Subbiah and Asija 1956). Available phosphorus in sample with low pH ($\leq$5) was determined using Bray and Kurtz method employing ammonium fluoride as extractant, whereas, Olsen method was used for sample with high pH ($\geq$7) using sodium bi-carbonate as extracting agent (Singh *et al.* 2007). A 1 (M) solution of ammonium acetate was used to extract available potassium from samples. The concentration of the extracted potassium was determined using flame photometer (Singh *et al.* 2007). Prior to the determination of total heavy metal (Al, Ba, Mo, Pb, Se, Si, and Sr) content, ash samples were digested in a microwave (Mars 5, CEM). Following the US EPA 3051A method (US EPA 2007), the metal concentration in the acid digestate was determined using Atomic Absorption Spectrophotometer (SOLAAR, TJA Solution, UK). The above-mentioned methodologies were also used earlier for characterizing the control samples, which were collected from each study site before the reclamation activities started, i.e., at zero time.

Statistical Analysis

Observation on each physicochemical parameter, microbial biomass, dehydrogenase activity, total phenolics, and total metal were analysed using SPSS (SPSS Inc., version

Table 1 Details of study sites

Location	Climate	Area reclaimed (sq. meter)	Plants used	Amendments used	Reclamation activities started
Badarpur Thermal Power Station, Delhi, India (S1)	Monsoon-influenced humid subtropical RF (mm): 689 Temp (°C): 2–47	3900	*Dalbergia sissoo, Eucalyptus tereticornis, Melia azadirachta, Populus deltoides, Helianthus annuus, Polianthes tuberosa, Tagetes erecta*	Farm yard manure (FYM) and mycorrhizal bio-fertilizer	1998
Korba Super Thermal Power Station, Chhattisgarh, India (S2)	Hot temperate RF (mm): 952 Temp (°C): 15–45	33760	*Shorea robusta, Tectona grandis, Dilbergia sissoo, Albizia procera, Casuarina equisetifolia, M. azadirachta, Dendrocalamus strictus, Populus euphratica, Eucalyptus tereticornis, Bombex ceiba, Gmelina arborea, Polianthes tuberosa*, *Helianthus annuus, Tagetes erecta, Mentha arvensis*, *Vetiveria zizanoides, Agave sisalana*		1999
Vijayawada Thermal Power Station, Andhra Pradesh, India (S3)	Tropical wet and dry RF (mm): 1219 Temp (°C): 15–47	40000	*Jatropha curcas, Parkinsonia aculeata, Aloe vera, Vetiveria zizanioides*		2003

*RF represents annual average rainfall (2006–2010); Temperature indicates annual average min - max

Table 2 Physicochemical properties (Mean ± SE) of control (zero time, n = 3) and reclaimed ash (n = 20)

	Badarpur (S1)		Korba (S2)		Vijayawada (S3)	
Parameters	Control	Reclaimed ash	Control	Reclaimed ash	Control	Reclaimed ash
pH	7.41 ± 0.01	7.42 ± 0.17	7.97 ± 0.09	5.57 ± 0.06*	8.39 ± 0.01	8.086 ± 0.07
EC (dSm^{-1})	1.13 ± 0.04	1.73 ± 0.24*	0.4 ± 0.010	0.5 ± 0.06	0.16 ± 0.003	0.33 ± 0.03*
OC (%)	0.60 ± 0.01	1.99 ± 0.08*	0.21 ± 0.02	0.93 ± 0.09*	0.18 ± 0.008	0.45 ± 0.04*
Av N (%)	0.0010 ± 0.0001	0.007 ± 0.001*	0.001 ± 0.0001	0.007 ± 0.001*	0.0014 ± 0.0001	0.007 ± 0.001*
Av P (ppm)	11.7 ± 0.06	71.6 ± 2.1*	7.8 ± 0.29	45.7 ± 3.2*	13.6 ± 0.29	50.1 ± 4.0*
Av K (ppm)	111.9 ± 4.8	149.0 ± 3.9*	79.6 ± 8.9	42.2 ± 6.1	37.5 ± 2.7	104.9 ± 19.6*

*indicates significance difference at $p < 0.05$ according to independent samples T test.

16.0). Independent sample T-test was carried out to compare the means of control and sample at the significance level of 0.05.

RESULTS AND DISCUSSION

The comparison of different physicochemical properties and biological properties between ash collected from reclaimed sites and the control are presented in Table 2–3.

Alteration in pH was found in all three study sites, although the extent of changes varied widely among sites. Maximum alteration against control was found in S2 (from 7.97 to 5.57), followed by S3, and S1. All the three sites showed average increase in EC however in S2 it was not significant ($p < 0.05$). The factor responsible for the alteration in pH and EC may be the continuous changes in equilibrium between cations and anions present in the ash. Among three sites, there was a sharp increase in Al content at S2 (Table 3), suggesting a strong Al hydrolysis ($Al^{3+} + H_2O = Al\ (OH)^{2+} + H^+$) effect that led to a marked drop in pH (Sparks 2003). The increase in EC may be due to dissolution reactions over time from the ash materials and also accumulation of salts from underground to surface due to capillary action (Carrow and Duncan 2004). At the same time, chloride accumulation on the surface ash due to capillary action may be responsible for increases in EC. In addition, the physical and chemical properties of fly ash vary widely depending on the coal type, boiler type, ash content in coal, combustion method, and collector setup (Basu *et al*. 2009).

Table 3 Comparison of total metal content (Mean ± SE, mg/kg) in control ash (zero time, n = 3) and reclaimed ash samples (n = 20)

	Badarpur (S1)		Korba (S2)		Vijayawada (S3)	
Parameters	Control	Reclaimed ash	Control	Reclaimed ash	Control	Reclaimed ash
Al	6479 ± 250	5581 ± 289	461 ± 16	1504 ± 149*	6130 ± 125	3178 ± 383*
Ba	588 ± 24	629 ± 15	153 ± 5	232 ± 14*	289 ± 6	293 ± 21
Mo	38.8 ± 0.8	29.5 ± 1.1*	18.3 ± 0.4	17.8 ± 0.3	21.5 ± 0.5	18.7 ± 1.0
Pb	9.8 ± 0.7	11.4 ± 0.8	15.3 ± 0.3	17.2 ± 0.4	23.1 ± 1.1	21.6 ± 0.5
Se	16.6 ± 0.5	25.8 ± 2.9*	26.6 ± 0.4	46.4 ± 3.8*	13.8 ± 0.5	42.8 ± 3.5*
Si	184 ± 6.7	161 ± 17	104 ± 4.7	273 ± 37*	398 ± 7.7	361 ± 25
Sr	8.3 ± 0.5	7.4 ± 0.5	1.2 ± 0.1	1.5 ± 0.1	18.5 ± 0.5	8.9 ± 1.5*

*indicates significance difference from control at $p < 0.05$ according to independent samples T test

Consequently, variations in weathering processes are also expected in ash derived from different sources.

OC in reclaimed ash (0.45–1.99%) found significantly ($p < 0.05$) higher than control (0.18–0.60%). Continuous litter fall from established plant species and natural decomposition of the same may be responsible for increase in organic carbon in reclaimed ash. In addition, vegetation cover also decreases the risk of soil erosion and can restore the soil's organic matter (Sinoga *et al*. 2012)

Available nitrogen is directly associated with organic carbon and hence like OC, significant increase ($p < 0.05$) in available nitrogen was found in samples from reclaimed ash ponds.

Available phosphorus content was found to be significantly higher ($p < 0.05$) in reclaimed ash, which may be due to the phosphate solubilisation activities of mycorrhiza added during plantation activities.

A mixed result was found in case of potassium (K): as compared to control, S1 and S3 were found to have significantly higher ($p < 0.05$) K content, whereas. S2's content was lower but not significant. Various factors including weathering, upward journey of soluble ions through capillary action, contribution from degradation of plant litters may be responsible for such typical variation of K content in different sites.

Total phenolics content in reclaimed ash pond was found significantly higher ($p < 0.05$) than control (Figure 1). Increase in phenolic contents in the reclaimed ash is due to an increase in humus content from leaf litter and organic debris from established plant species.

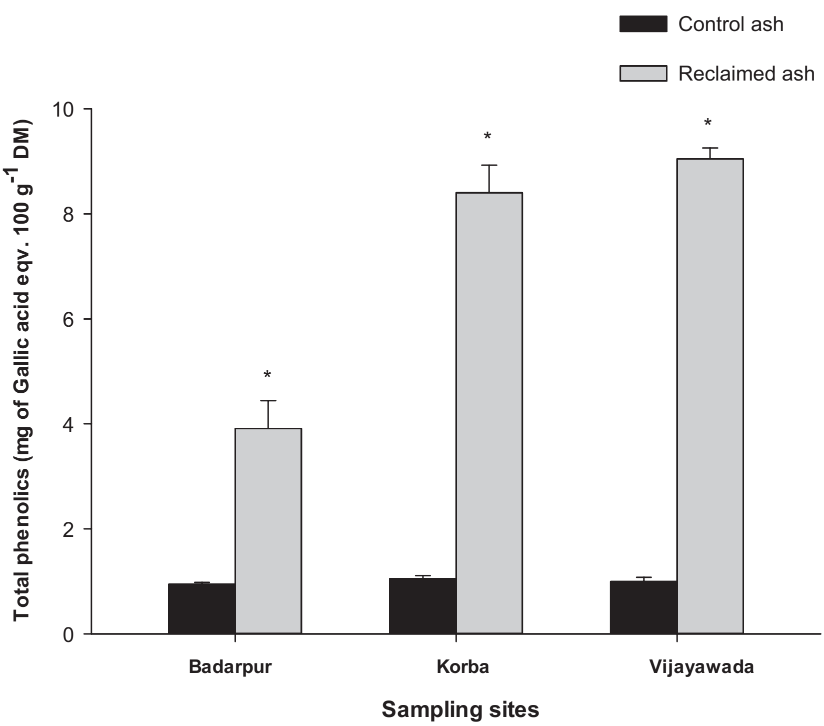

Figure 1 Improvement in the total phenolic content of pond ash reclaimed through green cover development (Each error bar indicates Standard Error, and * indicates significant difference from control at $p < 0.05$).

Phenolics are secondary metabolites and have a marked effect in plant-soil systems. They function as part of the structural plant matrix, act as constitutive protection against invading organisms, affect cell and plant growth, and are structural and functional components of soil organic matter. Besides, they also regulate the residue decomposition rate, nutrient release from plant residues in soil and increase long-term soil structure (Martens 2002).

The microbial biomass of soil is defined as the part of the organic matter in the soil that constitutes living microorganisms smaller than the 5–10 micron and is an indicator of soil health. Due to the dominant contribution in soil metabolism and its importance as a sink and source of nutrients for plants, microbial biomass is considered one of the main determinants of soil fertility (Logah *et al.* 2010). Microbial biomass in reclaimed ash was found to be much higher than the control, indicating significant ($p < 0.05$) improvements in the fertility of the ash in reclaimed ponds (Figure 2). The relatively lower microbial activity at S2 site may be due to higher Al content and lower pH. At acidic environment, Al becomes more soluble and potentially toxic to microorganisms (Wood 1995).

Dehydrogenase is a respiratory enzyme, and is an integral part of all soil organisms. It gives a measure of biological activity of soil at a given time. Soil microorganisms use dehydrogenase for various metabolic activities and for breaking down organic matter in soil. Significantly higher ($p < 0.05$) dehydrogenase activities were found in reclaimed ash ponds than in the control. Higher dehydrogenase activity indicates higher overall microbial activities (Dick 1997) (Figure 3).

No particular trend was found in alteration of total heavy metal content in reclaimed ash due to establishment of green cover over the abandoned ash pond (Table 3). In S1, concentration of Mo was found to be significantly ($p < 0.05$) lower than control but the

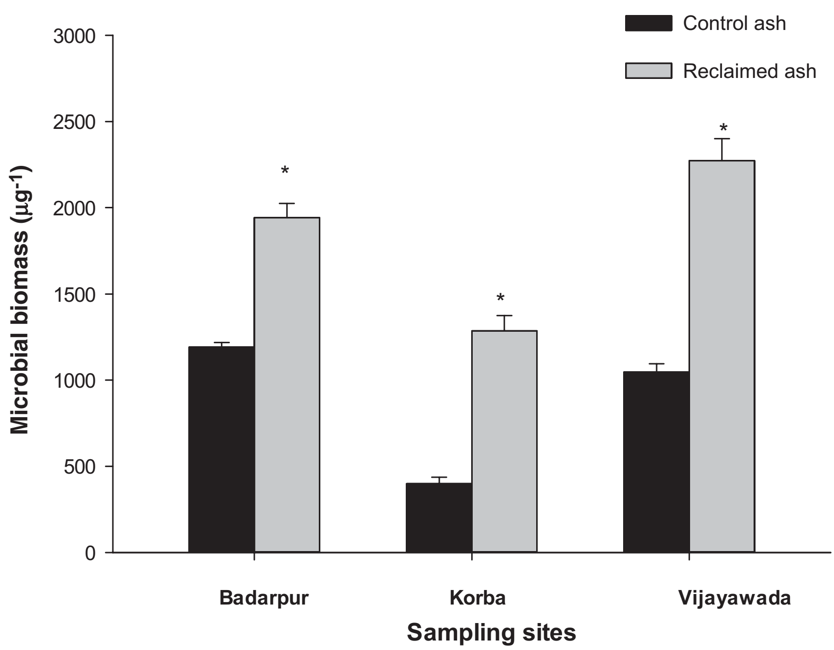

Figure 2 Increase in microbial biomass in pond ash due to development of green cover (Each error bar indicates Standard Error, and * indicates significant difference from control at $p < 0.05$).

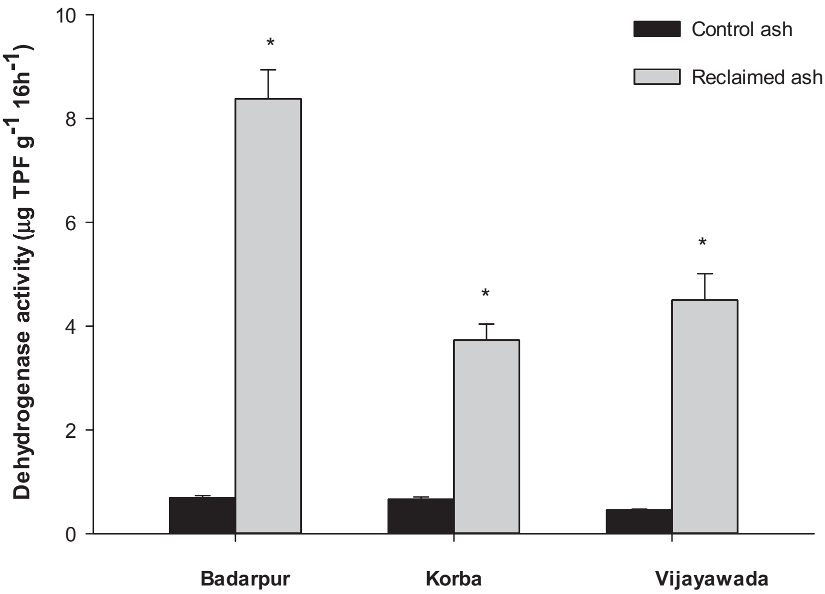

Figure 3 Enhanced dehydrogenase activities in reclaimed ash due to establishment of vegetation over it (Each error bar indicates Standard Error, and * indicates significant difference from control at $p < 0.05$).

opposite was true for Se. Concentration of Al, Ba, Se, and Si were found to be significantly higher ($p < 0.05$) in reclaimed ash from S2. Significantly lower ($p < 0.05$) concentration of Al and Sr were found in reclaimed ash of S3 as compared to the control, whereas Se was found to be lower in the control. It is quite difficult to explain such severe variations in total heavy metal contents in different sites based on a few factor like pH (lower the pH higher the mobility of metals) and presence of phenolic compounds (higher the phenolic compounds higher will be organo-metal complexes and hence higher will be availability of metals (Mulder and Cresser 1994)). Different communities of plant species used, age of sites, local climatic conditions may all partly be responsible for such wide variations.

CONCLUSION

The results pointed out that development of green cover on abandoned ash pond leads to not only conversion of barren grey land to an aesthetically pleasing landscape but also improves the physicochemical and biological properties of ash. It can increase the organic matter (2.5–4.5 fold) and microbial activities (6–12 fold) significantly, which is essential for further establishment of native flora and improvement of existing ecosystem. Considering the effectiveness of present reclamation technology, it can also be explored for reclamation of other waste dumps.

However, the extent of improvement in properties of ash also depends on various other factors including age of the dump, climatic conditions of the regions and plant species used for reclamation activities. Thus, to understand the change cycle more precisely, more extensive and continuous study on the same site year after year is required.

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