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ARTICLE

Effect of Elevated [CO₂] and Nutrient Management on Grain Yield and Milling Quality of Rice in Subtropical India

Poonam Biswal  Dillip Kumar Swain *

Agricultural and Food Engineering Department, Indian Institute of Technology Kharagpur, Kharagpur, 721302, India

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ABSTRACT

The climate change due to mingled effect of rising [CO₂] level and temperature will influence crop production by affecting various components of the production system. In the present study, Open Top Chamber (OTC) facility has been used to realize the consequence of rising [CO₂] with nutrient management on rice crop. The experiment was organized in open field and inside OTC with ambient [CO₂] (400 ppm) and elevated [CO₂] (25%, 50% and 75% higher than ambient) in wet season of the year 2017-18 at Kharagpur, India. Increase in [CO₂] level resulted decreasing trend in growth, yield attributes (filled grains number) and grain yield. The nutrient management with use of only chemical fertilizer at recommended dose gave highest grain yield, which was comparable with integrated management using chemical and biofertilizer. Post-harvest processing quality such as head rice percentage and the head rice yield decreased significantly with CO₂ elevation. The elevated [CO₂] with 25 to 75% higher than ambient, reduced the head rice percentage by 13 to 21 %. The research stated that investigations on climate change adaptations should be made to avoid the negative impact of rising [CO₂] level and temperature on crop yield and processing quality.

1. Introduction

Climate change and its variability is a major issue and has greater impact on global food production. Along with this, growing population and increasing demand for food is a threat for survival of upcoming generations. Due to rising levels of greenhouse gases mainly [CO₂], temperature is increasing and causes uncertainty in rainfall, which further has both absolute and erratic effect on global food production [13]. Increasing atmospheric [CO₂] influences all the physiological process in plants, and are expected to influence the growth and yield of the crop, composition of grains, and post-harvest qualities of grains.

According to previous studies, rising atmospheric [CO₂] level increased yield of food grains in absence of temperature increase [2, 18]. Rice being C3 crop, behaves positively with increasing atmospheric [CO₂] due to increasing carbon assimilation rates. But the combined effect of erratic rainfall and rising temperature will have variable effect on the production. Rising temperature with atmospheric [CO₂] elevation increases respiration rate in plants, which is likely to affect the yield of food grain under [CO₂] elevation. The temperature rise diminishes the absolute effect of rising [CO₂] level on grain yield of cereal crops [16, 17]. As rice crop is very sensi-
to study the effect of elevated \([\text{CO}_2]\) with varying nitrogen. In view of this, the present investigation was formulated for meeting the crop demand under varying environment. Treatments to maintain the available nutrients in the soil of rice. Hence, it is necessary to adapt nutrient management in OTC experiment on grain yield and milling qualities of rice.

According to previous studies, increasing level of \([\text{CO}_2]\) increased soil microbial use of N, which resulted in decreasing soil available N \([10]\). Decreasing soil available N influences crop growth, yield, and post-and processing qualities. Insufficient nutrient supply and high temperature affects the grain quality of rice and produces chalky grains which breaks very easily while undergoing the process of milling. It has been observed that higher amount of nitrogen increases the grain hardness and provide resistance from deterioration during the process of milling \([14]\). Open Top Chambers (OTCs) are the most widely used and accurate method for exposing field-grown crops to elevated \(\text{CO}_2\) and other atmospheric gases \([20]\). There is limited research on the effect of nutrient management and elevated \([\text{CO}_2]\) on growth, yield and processing quality of rice. Hence, it is necessary to adapt nutrient management treatments to maintain the available nutrients in the soil for meeting the crop demand under varying environment. In view of this, the present investigation was formulated to study the effect of elevated \([\text{CO}_2]\) with varying nitrogen management in OTC experiment on grain yield and milling qualities of rice.

2. Materials and Methods

2.1 Experiment Site

The field experiment was performed in the research farm of Agricultural and Food Engineering Department, Indian Institute of Technology Kharagpur, Kharagpur (22°19’N latitude and 87°19’E longitude). The soil of the field experimental site is red lateritic type with sandy loam in texture. The relevant soil properties are low available N content, available K content, and organic C with medium available P content. The location meet with an average annual rainfall of 1500 mm having humid and subtropical climate. The average maximum and minimum temperature ranges from 25°C in December/January to 38°C in April/May and 15°C in December/January to 25°C in June, respectively.

2.2 Experimental Details

The experiment was conducted in open field and inside OTCs in wet season of the year 2017-18. The OTCs made up of polycarbonate sheets having at least 80% light transmitting capacity, were used to build microhabitats with different environmental conditions (ambient and elevated). The treatment details including environmental conditions and nutrient management are explained below:

Factor 1: Environmental conditions (E)
(1) Open Field (OF): Open field under ambient conditions
(2) OTC(Amb \(\text{CO}_2\)): OTC along with ambient level of \([\text{CO}_2]\) (= 400 ppm)
(3) OTC(+25% \(\text{CO}_2\)): OTC along with 25% higher \([\text{CO}_2]\) level than OTC(Amb \(\text{CO}_2\)) (= 500 ppm)
(4) OTC(+50% \(\text{CO}_2\)): OTC along with 50% higher \([\text{CO}_2]\) level than OTC(Amb \(\text{CO}_2\)) (= 600 ppm)
(5) OTC(+75% \(\text{CO}_2\)): OTC along with 75% higher \([\text{CO}_2]\) level than OTC(Amb \(\text{CO}_2\)) (= 700 ppm)

Factor 2: Nutrient management (N)
(1) N0-Control (no application of fertiliser)
(2) N(CF100)- Application of 100% recommended dose (N, P and K) of Chemical fertilizer (CF)
(3) N(CF50 + BF50)- Application of 50% recommended dose (N, P and K) of CF with 50% N recommendation of Bio fertilizer (BF); Integrated nutrient management
(4) N(BF100)-BF at 100% N recommendation

The fertilizer application for CF100 was done on the basis of recommendation (N: P\(_2\)O\(_5\): K\(_2\)O - 100:50:60 kg ha\(^{-1}\)). The BF source was blue-green algae, which was cultivated in the research farm. The blue-green algae as BF100 was applied at 1 t ha\(^{-1}\). In all the experimental plots except N0 (control), P\(_2\)O\(_5\) and K\(_2\)O were applied full as basal through the application of single super phosphate and muriate of potash, respectively. The source of N for CF was urea, which was applied in three equal splits i.e. planting, tillering and panicle initiation. The Nitrogen requirement For BF100, blue green algae were used as per fresh weight which contains 4% N. The BF was applied in four splits in 15-20 days interval from transplanting.

The four N management treatments were applied in each environmental condition with two replications. The experiment was conducted in a split-plot design, where environmental conditions were in main plot and N management in sub-plot of the design.
2.3 Experimental Setup and Instrumentation

There were four OTCs and one open field and each of them were divided into eight sub-plots of size 1.8m × 1m. Carbon dioxide monitors, relative humidity sensors, and temperature probes were used to continuously check the level of [CO₂], relative humidity, and air temperature, respectively. Elevation of [CO₂] inside OTC was guarded by computer aided SCADA (Supervisory control and data acquisition) system. The system controlled the flow of CO₂ as per the desired level of [CO₂] inside OTC and data were logged on daily basis at 1 min time lapse. Whenever the level of [CO₂] was lower than the desired level, the system passes a command for releasing CO₂ into the OTC. The release of CO₂ was automatically stopped when the flow of CO₂ reaches the desired level. The [CO₂] level for open field was about 400 ppm, and was maintained accordingly at 25%, 50% and 75% higher than in the open field for OTC with elevated [CO₂] through the computerized real system.

2.4 Crop Management

The popular rice cultivar IR36 was selected for the experiment. Tillage operations in the experimental field were performed 10 days prior to transplanting and puddled 5 days before transplanting. The seedlings of 25 days were transplanted on 14 July 2017 with row and hill spacing 20 cm and 15 cm, respectively using 2 seedlings per hill. Irrigation was given at the critical growth stages and whenever required to maintain saturation throughout.

2.5 Plant Sampling for Biomass Partitioning

Tiller numbers of twenty hills of each plot were noted, and average tiller number of illustrative hill was established at every 20 days interval till harvesting. The representative hill was treated as sample hill, and detached into leaves, stems, and panicles. The separated parts were stored in an oven for drying at 70°C till constant weight was recorded. The dry weight of stem, leaf and panicles were taken.

2.6 Yield Attributes and Grain Yield

Plants were harvested from 150cm × 60cm area at the centre of each experimental plot to evaluate the grain yield of rice. The total number of panicle in the selected area was assessed and two illustrative hills were selected to determine the filled grain number for each panicle. The required observations for other yield attributes were also recorded. The grains were then separated from the harvested plants of the selected area to get the grain and straw yield for each experimental plot.

2.7 Rice Milling Quality

200g of cleaned and air-dried grain samples were collected from the harvested grains of each plot and stored for a month at ambient condition before milling, for further analysis of processing qualities. Rubber Roll Sheller was used for dehulling the rice grains to produce brown rice (BR), and then milled with rice polishing machine to calculate percentage of brown rice [22]. The degree of polish, brown rice percentage (BRP), milled rice percentage (MRP) and head rice percentage (HRP) were calculated after separation of head and broken rice. The brown rice yield (BRY), milled rice yield (MRY) and head rice yield (HRY) was calculated by multiplying each of them with rough rice yield [20].

Degree of polish (DP) = \( \frac{\text{weight of bran (g)}}{\text{weight of brown rice (g)}} * 100 \)

\[ \text{BRP} = \frac{\text{weight of brown rice (g)}}{\text{weight of rough rice (g)}} * 100 \]

\[ \text{MRP} = \frac{\text{weight of milled rice (g)}}{\text{weight of rough rice (g)}} * 100 \]

\[ \text{HRP} = \frac{\text{weight of head rice (g)}}{\text{weight of rough rice (g)}} * 100 \]

2.8 Statistical Analysis

The experiment was conducted in a split plot design with 20 treatment combinations [environmental conditions (5) × nutrient management (4)] and two replications. The significance of factors was tested for each observations at p=0.05 by preparing Analysis of variance (ANOVA) of the observed data. Evaluation of treatment effects is done by calculating Least significant difference (at p=0.05) among the treatment means.

3. Results and Discussion

3.1 Above Ground Biomass

The observations for above ground biomass including leaf, stem and panicle at 60 DAT (Days after transplanting) are shown in Table 1. Rising atmospheric [CO₂] lev-
el up to 75% above ambient increased the above ground biomass up to 32%, though they were comparable. Increasing [CO₂] level 25% above ambient resulted in increased biomass of rice by 13%[19]. It has been also stated that rice crops grown at 570 ppm acquired biomass faster than those grown under ambient [CO₂] during critical stages[8]. Rising [CO₂] level accelerates photosynthesis and thus resulted in more biomass production. It has been stated that increased biomass under elevated [CO₂] is mainly due to increased net assimilation capacity and photosynthesis rate by stimulating carboxylation and retarding oxygenation of ribulose bisphosphate carboxylase[15]. The nutrient management had significant effect on biomass accumulation of rice. The recommended dose of chemical fertilizer (CF100) gave significantly (p<0.05) highest above ground biomass followed by integrated nutrients (CF50+BF50). The nutrient management treatments with full dose through chemical fertilizer or integration of bio and chemical source met the N requirement of the crop, hence increased the biomass production. However the application of biofertilizer alone was not effective to supply the desired quantity of nutrient for rice production.

3.2 Filled Grains Number and Grain Yield

The elevation of [CO₂] in OTC by 25%, 50% and 75% increased the mean air temperature by 0.62°C, 1.75°C, and 2.12°C, respectively as compared to ambient environment. The increasing [CO₂] level decreased the number of filled grains as compared to ambient due to the negative effects of temperature associated with stomatal closure, which resulted in less number of filled grains. The adverse effect of high temperature becomes maximum when it coincides with flowering and grain-filling period[8]. Our results indicated that rising [CO₂] level above ambient by 25%, 50% and 75% decreased filled grains number significantly (p<0.05) (Table 1). Increase in temperature will affect rice growth and spikelet formation leading to grain yield reduction[21]. The elevated [CO₂] alone may increase the grain yield mainly because of more number of tiller production, but the associated higher temperature induces spikelet sterility, hence reduced the grain yield. We observed that rising [CO₂] level up to 75% above ambient decreased the grain yield up to 19%. The recommended dose of chemical fertilizer (CF100) gave significantly (p<0.05) highest filled grains number and grain yield followed by integrated nutrients (CF50+BF50). As CF100 and CF50+BF50 produces more biomass, hence resulted in more filled grains number and grain yield.

3.4 Rice Processing Quality

Increase in [CO₂] level by 25%, 50% and 75% above ambient did not bring any significant change in BRP and MRP, but decreased HRP significantly (Figure 1). According to many reports, rising temperature when coincides with critical stages like flowering and maturity, resulted in poor grain appearance and reduced milling qualities due to increased chalkiness in rice grains, which further reduces the head rice yield[3,4,7]. The chalkiness in rice grain reduces the head rice yield due to more broken rice. Our study indicated that [CO₂] level 25 to 75% higher than ambient reduced the head rice percentage by 13 to 21%. Increase in [CO₂] level by 75% above ambient, resulted a significant decline in BRY. However, the HRY was decreased significantly (p<0.05) even with 25% increase in [CO₂] level above ambient. Further increase in [CO₂] level (≥50%) did not bring any significant changes in HRY (Table 2). The recommended dose of chemical fertilizer (CF100) had significantly (p<0.05) higher HRP and HRY as compared to other three nutrient management practises. Moreover, the adverse effect of elevated [CO₂] on HRY was lower in CF100 as compared to rest nutrient management treatments. According to previous studies, higher amount of nitrogen increases the grain hardness and provide resistance from deterioration during the process of milling[14]. Insufficient N supply and high temperature affected the process of milling, thus decreased the HRY. The CF100 had higher amount of nitrogen availability in soil for crop uptake as compared to the other treatments, hence was least affected from the [CO₂] elevation.

4. Conclusions

From the study, it can be understood that increasing atmospheric [CO₂] favoured leaf and stem biomass accumulation, but affected the grain formation and post-harvest milling quality of rice. Increasing atmospheric [CO₂] level by 25% or higher than the ambient, though had no significant effect on grain yield, but affected the head rice percentage significantly, thereby reduced the processed rice yield. With the [CO₂] elevation by 25 to 75%, the head rice percentage was lowered by 13 to 21% as compared to the ambient environment. The adverse effect, however, can be minimized by improving nutrient management in the rice crop. This study stated that a detailed investigation on nutrients management is required for developing suitable adaptations to the climate change.
Supplements

Table 1. Effect of environment and nutrient management on above ground biomass at peak growth stage, filled grains per panicle and grain yield of rice

<table>
<thead>
<tr>
<th>Environment</th>
<th>Above ground biomass (kg/ha)</th>
<th>Filled grains number per panicle</th>
<th>Grain yield (kg/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OF</td>
<td>4250</td>
<td>73</td>
<td>2820</td>
</tr>
<tr>
<td>OTC(Amb CO₂)</td>
<td>3633</td>
<td>105</td>
<td>2892</td>
</tr>
<tr>
<td>OTC(+25% CO₂)</td>
<td>3731</td>
<td>79</td>
<td>2553</td>
</tr>
<tr>
<td>OTC(+50% CO₂)</td>
<td>4248</td>
<td>84</td>
<td>2443</td>
</tr>
<tr>
<td>OTC(+75% CO₂)</td>
<td>4789</td>
<td>77</td>
<td>2343</td>
</tr>
<tr>
<td>SEm±LSD (p=0.05)</td>
<td>326</td>
<td>5</td>
<td>106</td>
</tr>
<tr>
<td>Nutrient management</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N0</td>
<td>2893</td>
<td>67</td>
<td>1842</td>
</tr>
<tr>
<td>N(CF100)</td>
<td>6341</td>
<td>107</td>
<td>3439</td>
</tr>
<tr>
<td>N(CF50+BF50)</td>
<td>4445</td>
<td>91</td>
<td>3180</td>
</tr>
<tr>
<td>N(BF100)</td>
<td>2842</td>
<td>78</td>
<td>1980</td>
</tr>
<tr>
<td>SEm±LSD (p=0.05)</td>
<td>291</td>
<td>4</td>
<td>408</td>
</tr>
</tbody>
</table>

Note: CF-Chemical Fertilizer, BF-Biofertilizer, OF-Open Field, OTC-Open Top Chamber, SEm-Standard Error of mean, LSD- Least Significant Difference, NS- Not Significant.

Table 2. Effect of environment and nutrient management on Brown Rice Yield (BRY), Milled Rice Yield (MRY) and Head Rice Yield (HRY)

<table>
<thead>
<tr>
<th>Environment</th>
<th>BRY, kg/ha</th>
<th>MRY, kg/ha</th>
<th>HRY, kg/ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>OF</td>
<td>1731</td>
<td>1389</td>
<td>992</td>
</tr>
<tr>
<td>OTC(Amb CO₂)</td>
<td>1643</td>
<td>1348</td>
<td>1008</td>
</tr>
<tr>
<td>OTC(+25% CO₂)</td>
<td>1688</td>
<td>1484</td>
<td>803</td>
</tr>
<tr>
<td>OTC(+50% CO₂)</td>
<td>1717</td>
<td>1333</td>
<td>819</td>
</tr>
<tr>
<td>OTC(+75% CO₂)</td>
<td>1555</td>
<td>1282</td>
<td>843</td>
</tr>
<tr>
<td>SEm±LSD (p=0.05)</td>
<td>23</td>
<td>80</td>
<td>42</td>
</tr>
</tbody>
</table>

Note: CF-Chemical Fertilizer, BF-Biofertilizer, OF-Open Field, OTC-Open Top Chamber, SEm-Standard Error of mean, LSD- Least Significant Difference, NS- Not Significant.

References


[5] “Crops/Regions/World list/Production Quantity (pick lists), Rice (paddy), 2014”


ARTICLE

Warming Changed Soil Respiration Dynamics of Alpine Meadow Ecosystem on the Tibetan Plateau

Junfeng Wang\textsuperscript{1,2,4,5} Ziqiang Yuan\textsuperscript{1*} Qingbai Wu\textsuperscript{1} Rashad Rafique\textsuperscript{3}

1. School of Environmental Science and Technology, Shanxi University of Science & Technology, Xi’an, Shanxi, 710021, China
2. State Key Laboratory of Frozen Soil Engineering, Cold and Arid Regions Environmental and Engineering Research Institute, Chinese Academy of Sciences, Lanzhou, Gansu, 730000, China
3. Joint Global Change Research Institute, Pacific Northwest National Lab, College Park, MD 20740, USA
4. Department of Microbiology and Plant Biology, University of Oklahoma, Norman, OK 73019, USA
5. Beiluhe Observation Station of Frozen Soil Environment and Engineering, Cold and Arid Regions Environmental and Engineering Research Institute, Chinese Academy of Sciences, Lanzhou, Gansu, 730000, China

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ABSTRACT

Alpine meadow system underlain by permafrost on the Tibetan Plateau contains vast soil organic carbon and is sensitive to global warming. However, the dynamics of annual soil respiration ($R_s$) under long-term warming and the determined factors are still not very clear. Using open-top chambers (OTC), we assessed the effects of two-year experimental warming on the soil CO$_2$ emission and the Q$_{10}$ value (temperature sensitivity coefficient) under different warming magnitudes. Our study showed that the soil CO$_2$ efflux rate in the warmed plots were 1.22 and 2.32 times higher compared to that of controlled plots. However, the Q$_{10}$ value decreased by 45.06% and 50.34% respectively as the warming magnitude increased. These results suggested that soil moisture decreasing under global warming would enhance soil CO$_2$ emission and lower the temperature sensitivity of soil respiration rate of the alpine meadow ecosystem in the permafrost region on the Tibetan Plateau. Thus, it is necessary to take into account the combined effect of ground surface warming and soil moisture decrease on the $R_s$ in order to comprehensively evaluate the carbon emissions of the alpine meadow ecosystem, especially in short and medium terms.

1. Introduction

Alpine zones are usually characterized with a long seasonal surface soil freezing and a short vegetation period. Soil organic carbon stored in the alpine soils is huge due to low decomposition rates\textsuperscript{[22,23]}. However, these regions would be undergone severe impact due to a higher rate of temperature increase under global warming\textsuperscript{[17]}. For the Tibetan Plateau, the alpine meadow ecosystem with $6.37\times10^5$ km$^2$ area, (~50 % of total alpine grassland area) holds $11.3$ Pg of carbon (C)\textsuperscript{[35]}. The C loads in the alpine

*Corresponding Author:
Ziqiang Yuan,
State Key Laboratory of Frozen Soil Engineering, Cold and Arid Regions Environmental and Engineering Research Institute, Chinese Academy of Sciences, Lanzhou, Gansu, 730000, China;
Email: wangjf2008@lzb.ac.cn

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soils are significantly higher compared to those in the warmer soils\[10]. Therefore, any small change in this soil C pool can possibly trigger the atmospheric CO\(_2\) concentration surging and thus the dynamics of global climate\[2,7,9,12,13,18,44\].

Since 1850, the world mean temperature has been rising and will increase by a further 1.8 – 4.0 °C by the end of this century\[29,42,17\]. The temperature of the ecological alpine zone of the Tibetan Plateau has also been rising at a rate of 0.32 °C/10\(a\) in the recent 30 years\[26,39\]. Moreover, study predicted that this region would experience greater warming in the future\[17\]. So future climatic warming will trigger a sharp release of this C reservoir by \(R_s\), thereby altering the alpine meadow ecosystem from a net carbon sink to a net source of atmospheric CO\(_2\)[1,5,55]. Studies also have shown that climate warming would reduce species richness in alpine meadows and alter the above- and belowground productivity of the Tibetan Plateau\[20,21\].

To understand the mechanisms controlling soil respiration of the alpine meadow ecosystem, many experimental studies have been conducted in-situ\[5,8,33,22,55\]. However, the results are significantly different from site to site. Most of the investigations focus on the temperature dependency of C mineralization and evaluate \(Q_{10}\)\[1,5,41\]. A little information on the role of soil moisture in controlling \(R_s\) also exists\[7,9\], which is not enough to derive any specific relationship, especially when combined with near surface warming in high altitude regions (underlain by permafrost). In addition, the \(R_s\) during the growing seasons is well studied\[8,55\], but the temporal patterns of \(R_s\) in non-growing season and the determined factors are not very clear.

Therefore, in this research, we conducted a comprehensive experimental study to better understand the response of soil C under different warming magnitudes. We increased the near-surface air temperature with different amplitudes of the alpine meadow ecosystem on the Tibetan Plateau in situ for two years. The temporal variations of soil CO\(_2\) efflux rate, soil temperature and moisture at different depths, and correlations among them were examined carefully. Our objectives were to determine (1) how the \(R_s\) responded to warming with different temperature magnitudes (2) how the \(Q_{10}\) of \(R_s\) in the alpine meadow ecosystem changed as the amplitude of warming increased and (3) how the surface temperature and moisture of soil regulated \(R_s\) in the alpine meadow ecosystem underlain by permafrost.

2. Materials and methods

2.1 Study Site

The experiment was carried out in the Beiluhe region (34° 49′ 25.8″ N, 92° 55′ 45.1″ E), distributed with alpine meadow ecosystem, on the Tibetan Plateau (Figure 1). The study site is representative with an area about 151.6 km\(^2\) and the altitude ranges from 4600 m to 4800 m. The climate is frigid and dry with the frozen duration from October to April of the next year. The mean annual temperature is -3.60 °C and the annual precipitation is about 423.79 mm\[40\]. The dominant species are Kobresia pygmaea, K. humilis, Sergievskaja, K. capillifolia, and C. scabriostris\[40,54\].

![Figure 1. Location of the experimental site at the Beiluhe region on the Tibetan Plateau](image)

2.2 Experimental Setup

The experiment was carried out in a selected alpine meadow area, where the vegetation coverage was above 70%. We used a passive warming device, open-top chamber (OTCs), to create an artificially warmed environment\[32,50\]. In October 2010, five OTCs with height of 40 cm and coverage area of 0.98 m\(^2\) were installed. Five control plots with area of 1 m\(^2\) (100 cm × 100 cm) were also set up near the OTCs.

The air relative humidity and temperature at height of 20 cm above the near surface were determined (Vaisala HMP45AC, Finland) in both OTCs and control plots. Soil temperatures were measured at 5, 20, and 40 cm depths using thermistor sensors. The accuracy and resolution of these sensors were ± 0.05 °C and 0.01 °C respectively after calibrated. Soil moistures in the OTCs and control plots were also measured at the depths of 5, 20, and 40 cm using calibrated sensors (EC-5, Decagon USA). These measurements were automatically recorded with
a CR1000 datalogger (Campbell Scientific, Logan, UT, USA) at 1 h intervals. The distance between the OTCs and the control plots ranged from 8 m to 10 m. Thus three group plots with different temperature increments were established in the alpine meadow site: (1) alpine meadow plots with no warming treatment (Control), (2) alpine meadow plots with 40 cm-high OTCs treatment (OTC1), (3) alpine meadow plots with 80 cm-high OTCs treatment (OTC2). In each plot, a collar of 20 cm internal diameter and 10 cm height made with polyvinyl chloride (PVC) was inserted into the soil with 2 cm offset.

Soil CO$_2$ efflux rate was determined using a LI-8100A automated soil gas flux system (LI-COR, Lincoln, NE, USA). The live aboveground vegetation within the soil collars was pruned away 24 h prior to each measurement [24]. Soil CO$_2$ emission rate was measured with five replicate collars in each treatment plot. Measurement was carried out once every five days in the growing months (May - September) and every ten days in the non-growing months (January - April and October - December). For each measurement, the period between 09:00 and 12:00 h Beijing standard time (BST) was chosen to minimize daily variations in $R_s$. The $R_s$ was represented by the average of five replicates of each treatment and represented the daily mean soil CO$_2$ efflux.

2.3 Soil and Biomass Sampling and Analysis

At the start of the experiment in late October 2010, soil samples (100 cm$^3$) were collected randomly at the 0–10 cm and 10–20 cm depths beside each plot and stored in a refrigerator for further analysis. To determine the aboveground biomass, all the plants in a 0.25 m$^2$ area were clipped from the plot selected randomly and were stored with paper bags, and then were air-dried and weighted. To determine the belowground biomass, the soil and root were dug out above the 40 cm depth and weighted. To examine correlations among the air temperature, soil temperature and moisture, the $R_s$ the Pearson correlation was carried out. In addition, to test the dependency of $R_s$ on soil temperature and moisture, exponential regression was implemented. According to the regression analysis results, an exponential curve of the form was applied, where $y = t R_s$, $\beta_0$ and $\beta_1$ were fitted constants and $T$ was the 5 cm soil temperature. To compare dependency of $R_s$ on soil temperature in each warming treatment, $Q_{10}$ values were calculated, where $Q_{10} = e^{10*\beta_1}$. All tests were done at the 5% level of significance and all statistical analyses were performed with Origin software (Origin 8.0, OriginLab Corporation, USA).

3. Results

3.1 Property Difference between Treatment Plots

Statistical analysis found that the biomass and soil properties sampled beside the control, OTC1 and OTCs plots were similar (variability analysis, $F < 5$, $P = 0.05$) when the experiment was carried out (Table 1). In all plots, the soil bulk density, soil organic carbon, and total N content at the 10-20 cm depth were higher than those at the 0-10 cm depth. The belowground biomasses were much greater than those of aboveground.

### Table 1. Biomass and soil properties at the different warming treatment plots

<table>
<thead>
<tr>
<th>Variable</th>
<th>Depth (cm)</th>
<th>Control plots</th>
<th>OTC1 plots</th>
<th>OTC2 plots</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g cm$^{-3}$)</td>
<td>0–10</td>
<td>0.89 ± 0.2</td>
<td>0.87 ± 0.3</td>
<td>0.85 ± 0.4</td>
<td>n.s.</td>
</tr>
<tr>
<td></td>
<td>10–20</td>
<td>0.98 ± 0.1</td>
<td>1.01 ± 0.1</td>
<td>0.97 ± 0.2</td>
<td>n.s.</td>
</tr>
<tr>
<td>Soil organic C (kg m$^{-2}$)</td>
<td>0–10</td>
<td>0.48 ± 0.06</td>
<td>0.47 ± 0.04</td>
<td>0.51 ± 0.05</td>
<td>n.s.</td>
</tr>
<tr>
<td></td>
<td>10–20</td>
<td>1.32 ± 0.04</td>
<td>1.35 ± 0.02</td>
<td>1.29 ± 0.05</td>
<td>n.s.</td>
</tr>
<tr>
<td>Soil total N (g m$^{-3}$)</td>
<td>0–10</td>
<td>41.3 ± 7.2</td>
<td>40.1 ± 6.7</td>
<td>40.8 ± 5.9</td>
<td>n.s.</td>
</tr>
<tr>
<td></td>
<td>10–20</td>
<td>117.6 ± 12.8</td>
<td>119.4 ± 9.4</td>
<td>115.3 ± 10.4</td>
<td>n.s.</td>
</tr>
<tr>
<td>Above-ground biomass (kg m$^{-3}$)</td>
<td>0.33 ± 0.04</td>
<td>0.35 ± 0.02</td>
<td>0.32 ± 0.03</td>
<td>n.s.</td>
<td></td>
</tr>
<tr>
<td>Below-ground biomass (kg m$^{-3}$)</td>
<td>2.41 ± 0.4</td>
<td>2.37 ± 0.2</td>
<td>2.43 ± 0.3</td>
<td>n.s.</td>
<td></td>
</tr>
</tbody>
</table>

*Note: n.s.: no statistical significance; Values are means (n = 5) ± standard deviation (SD)*
3.2 Warming Effects on Air Temperature and Soil Hydrothermal Properties

The air temperatures between the OTC2, OTC1, and Control plots showed an obvious difference from each other at a 0.05 level (ANOVA, $F = 57$, $P = 0.001$). The warming magnitudes at the OTCs plots varied largely during the study period (Figure 2). Daily mean air temperature in the OTC2 and OTC1 plots were always higher than that in the Control plots. However, the near-surface air temperature in the OTCs and Control plots had a similar change trend. In general, the lowest of air temperature in all plots appeared in December and the highest occured in July.

Influenced by the air temperature rising in the OTCs plots, the soil temperatures at different measuring depths changed greatly (Figure 3). The larger magnitude of the temperature increased in the OTCs plots, the higher the soil temperature at different depths. The soil moistures in the OTCs plots also changed greatly due to the near-surface air temperature increase (ANOVA, $F > 23.08$, $P = 0.0001$). The higher the near-surface air temperature, the more decrease of the soil moisture content in the OTCs plots (Figure 4). The detailed impacts of experimental warming on the air temperature, soil temperature and soil moisture in this alpine meadow ecosystem can be referred to the authors’ published work [47].

Figure 2. Near-surface air temperature variations in the different warming treatment plots of an alpine meadow ecosystem for two years

Note: Air temperature values are means of five plots every day and the lines are plotted with the adjacent-averaging method. Black open squares, red open cycles, and blue open triangles are near-surface air temperatures in plots with different warming treatments. The corresponding solid lines with the same colors represent the mean variations in air temperatures.

Figure 3. Monthly variations of soil temperatures at 5, 20 and 40 cm depths in an alpine meadow ecosystem with different warming treatments.

Note: Soil temperature values are means of each month of two years in five plots. Bars represent the corresponding standard errors of the means.

Figure 4. Monthly variations of soil moistures at 5, 20 and 40 cm depths in an alpine meadow ecosystem with different warming treatments.

Note: Soil moisture values are means of each month of two years in five plots. Bars represent the corresponding standard errors of the means.
3.3 Dynamics of $R_s$ in Different Warming Treatment Plot

The dynamics of soil CO$_2$ efflux rate at different warming treatment plots are shown in Figure 5. The warming effects on $R_s$ appeared to be most pronounced during the warm seasons (May to September), where significant differences existed at a 99% confidence level ($p \leq 0.005$). In the cold seasons (January to April and October to December), the $R_s$ differed marginally among the OTC2, OTC1 and Control plots ($0.05 \leq p \leq 0.07$).

Figure 5. Variations of soil CO$_2$ efflux rate in an alpine meadow ecosystem with different warming treatments in two years

Note: Symbols are means (n = 5), and bars represent the corresponding standard errors of the means.

All the $R_s$ in the different warming treatment plots started to rise from April and reached to the maximum in August. Thereafter it began to decrease gradually and came to the minimum in December (Figure 5). In 2011, the monthly mean $R_s$ in the OTC2, OTC1 and Control plots attained their maximums of 5.9, 3.7 and 2.5 μmol m$^{-2}$s$^{-1}$, respectively, in August. Then they began to decrease gradually and came to the minimums of 0.6, 0.2 and 0.2 μmol m$^{-2}$s$^{-1}$, respectively, in December (Table 2). The dynamics of $R_s$ in 2012 was similar with that in 2011 but the maximums of $R_s$ in 2012 were much greater.

The difference of inter-annual variation in $R_s$ in different warming treatment plots was significant ($p \leq 0.05$). As the duration of experimental warming extended, the maximums of the $R_s$ showed an increase trend. For example, in 2011 the maximums of the monthly mean CO$_2$ efflux rate were 5.9 in the OTC2 plots and 3.7 μmol m$^{-2}$s$^{-1}$ in the OTC1 plots, but the corresponding maximums of $R_s$ in the OTC2 and OTC1 plots reached 11.2 and 8.3 μmol m$^{-2}$s$^{-1}$ in 2012 (Table 2). For the Control plots, the maximums of $R_s$ in 2011 and 2012 were 2.33 and 2.17 μmol m$^{-2}$s$^{-1}$, respectively. The $R_s$ also showed an obvious difference among different months for the same warming treatment during the experimental period (Table 2). In 2011, the annual amplitudes of $R_s$ were 5.38, 3.45 and 2.28 μmol m$^{-2}$s$^{-1}$, respectively, in the OTC2, OTC1 and Control plots. While in 2012, the corresponding annual amplitudes of $R_s$ in the OTC2, OTC1, and Control plots were 10.57, 7.87 and 2.99 μmol m$^{-2}$s$^{-1}$, respectively. The coefficients of temporal variation (CV) of $R_s$ in the OTC2, OTC1 and Control plots in 2011 and 2012 were 72.4, 76.7, 71.5% and 84.5, 83.2, 64.7%, respectively.

3.4 Impacts of Soil Temperature on $R_s$

For the alpine meadow ecosystem with different warming treatments, the dynamics of $R_s$ was regulated by the soil temperatures greatly and the $R_s$ showed a significant positive relation to the 5 cm soil temperature (Figure 6, $P < 0.05$). Soil temperature was an important explanatory variable in controlling the $R_s$ for the different warming treatments. By comparatively analyzing the $R_s$ among the different warming treatments (OTC2, OTC1, and Control) and

<table>
<thead>
<tr>
<th>Year</th>
<th>Treatment</th>
<th>Soils CO$_2$ flux (μmol CO$_2$ m$^{-2}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>OTC2</td>
<td>0.6±0.3</td>
</tr>
<tr>
<td></td>
<td>OTC1</td>
<td>0.2±0.4</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>0.2±0.3</td>
</tr>
<tr>
<td>2012</td>
<td>OTC2</td>
<td>0.6±0.2</td>
</tr>
<tr>
<td></td>
<td>OTC1</td>
<td>0.5±0.1</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>0.2±0.2</td>
</tr>
</tbody>
</table>

Note: Values are means (n = 5) ± SD
trol), it showed that the $R_s$ and the 5cm soil temperature had the same changing trend, and the higher the 5cm soil temperature increased, the greater the soil CO$_2$ efflux rate. At the OTC2 plots, the $R_s$ increased from 0.53 to 13.28 μmol m$^{-2}$ s$^{-1}$ as the 5cm soil temperature rose from -7.35 to 11.81 °C; while at the OTC1 plots, when the 5cm soil temperature increased from -9.29 to 10.96 °C, the corresponding $R_s$ increased from 0.19 to 10.06 μmol m$^{-2}$ s$^{-1}$. The CO$_2$ efflux rates at the OTC2 and OTC1 plots were 0.93 to 9.39 and 0.69 to 6.66 times greater than that at the Control plots, respectively.

Figure 6. Dynamics of $R_s$ and the 5cm soil temperature during the experimental period at the different warming treatment plots. Symbols are means (n = 5)

However, the inter-annual variations of $R_s$ at the experimental warming plots (OTC2 and OTC1) were significantly different between 2011 and 2012 although the 5cm soil temperatures changed gently inter-annually. As the experimental warming period extended, the soil CO$_2$ efflux rates showed an apparent increasing trend especially in the growing seasons (May to September) ($P < 0.05$). Experimental warming increased daily mean $R_s$ by 0.96 ~ 3.26 times in 2012 than that in 2011 at the OTC2 plots; at the OTC1 plots, the increase multiples of $R_s$ varied between 0.71 and 5.55. Whereas at the Control plots, the $R_s$ showed no significant interannual variation ($P > 0.05$).

The correlation of the 5cm soil temperature and the $R_s$ was fitted with an exponential model, which could explain 58 % – 65% of variations in soil respiration (Figure 7). As soil depth increased, the dependency of soil respiration on temperature declined ($P > 0.05$). The $Q_{10}$ values were 3.67, 4.06 and 7.39, respectively, at the OTC2, OTC1 and Control plots, which tended to decline as the amplitude of near-surface air temperature increased (Figure 7).

3.5 Impacts of soil moisture on $R_s$

The soil moisture also affected $R_s$ significantly in the alpine meadow ecosystem with different warming treatments ($P < 0.05$, Figure 8). In the Control, OTC1 and OTC2 plots, the dynamics of $R_s$ was with that of soil moisture at the 5cm depth during 2011 and 2012. By comparatively analyzing the soil moisture variations in the
Control, OTC1 and OTC2 plots, it showed that the more the soil moisture at 5 cm declined, the greater the $R_s$ increased. However, compared the variations of $R_s$ in 2011 with that in 2012, the soil CO$_2$ emission rate showed an obvious increasing trend under the condition that the 5cm soil moisture had no significant changes in the Control, OTC1 and OTC2 plots.

Figure 8. Dynamics of $R_s$ and the 5cm soil moisture during the experimental period in the different warming treatment plots. Symbols are means (n = 5).

Although the soil moisture decreased as the amplitude of the near-surface air temperature increased, the intensity and variation amplitude of $R_s$ improved. Correlation analysis indicated that the relationship between the $R_s$ and the 5cm soil moisture accorded with an exponential model ($y = a_0 e^{a_1 M}$) in the different warming treatment plots, where $y$ was the $R_s$, $a_0$ and $a_1$ were fitted constants and $M$ was the 5cm soil moisture. The model explained 64% – 68% of variations in soil respiration (Figure 9). As the soil deepened, the correlation of the $R_s$ and the soil moisture content weakened ($R^2 < 0.4$).

Figure 9. Correlation of the $R_s$ and the 5cm soil moisture during the experimental period in the different warming treatment plots (A-OTC2, B-OTC1, and C-Control).

4. Discussion

The ground surface was passively warmed by the OTCs via trapping solar radiation [45]. Although the OTCs had a warming effect both in the day and night, it primarily happened in the daytime due to the higher levels of solar radiation [30]. The amplitudes of the experimental warming treatments in this study were 6.33 (OTC2) and 2.96 °C (OTC1), respectively. Meanwhile, the temperature increments via the OTCs in our study were greater than that reported by the studies in the arctic region [31,36,48]. This may be attributed to the strong solar radiation on the Tibetan Plateau. In the OTCs plots, the greater air temperature increment resulted that the surface soil temperature increased much higher and the soil moisture content declined much greater in the experimental period. During our experimental warming, the increment of soil temperature at the 5cm depth was 0.61 – 5.72 °C, being similar with the study result in Northern Tibet by Lu et al [27]. The decrease in soil moisture of 11.8 – 20.5 % at the depth 5 cm was comparable with the reported studies [15,31,36,48].
This study showed quite a homogenous warming of the soil down to a depth of at least 40 cm, where more than 95% of the roots and most of the labile C in the organic layer were located. As a consequence, the increases of shallow soil temperature and a decrease of soil moisture would cause great impact on the $R_s$ of the alpine meadow ecosystem on the Tibetan Plateau.

Global warming was predicted to firstly cause effect on the C reservoir of the alpine and tundra ecosystems distributed in the high latitude and the high altitude regions [25]. It was reported that warming caused the $R_s$ to increase by 9.2 to 80% on the Tibetan Plateau [25,51]. Whereas, the increments of the $R_s$ in our study were by 232 and 122% in average at the condition of the near-surface warming by 6.91 and 3.59°C, respectively. The effect of $R_s$ promotion stimulated by warming in our study was more obvious compared with that reported elsewhere. This may be because the alpine meadow ecosystem on the Tibetan Plateau has adapted to the cold environment for a long time and is very sensitive to warming. Although the $R_s$ was very low (0.2 μmolm⁻²s⁻¹) in the control plots, the warming of the near-surface air temperature stimulated and accelerated the root respiration and the soil microbial respiration, which resulted in the soil CO₂ emitted intensely in the warming months. However, the mechanisms of how the experimental warming regulated the dynamics of the $R_s$ in the alpine meadow ecosystem still remains unclear due to the soil microbial respiration and the root respiration are difficult to be distinguish presently. So, much more detailed researches should be conducted to segregate the $R_s$ into microbial and root respiration. In addition, prolonged study periods are needed to elucidate the physiological responses of the components of $R_s$ to warming for the alpine meadow ecosystem on the Tibetan Plateau.

Most studies have shown that the $R_s$ was mainly controlled by the soil temperature and the soil moisture content, which were the two most important impact factors on the $R_s$ dynamics [6,27,52]. Our results also demonstrated that the $R_s$ under the different warming treatments correlated significantly to the soil temperature and the moisture content on the Tibetan Plateau ($p < 0.05, R^2 > 0.5$). The temperature sensitivity coefficient of $R_s$ was considered one of the most important parameters in evaluating the extent to which $R_s$ was affected by temperature [14]. The $Q_{10}$ values of $R_s$ in the different warming treatment plots at our experimental site were 3.67, 4.06 and 7.39 for the OTC2, OTC1, and Control, respectively. Our study demonstrated that the response of $R_s$ of the alpine meadow ecosystem on the Tibetan Plateau to near-surface warming was sensitive and rapid. The percentage of 58% – 65% variation in $R_s$ could be explained by the change of temperature. Whereas, the warming of the near-surface air temperature led to the decline in the $Q_{10}$, which suggested that the dependency of the $R_s$ on temperature decreased as the amplitudes of experimental warming rose in the alpine meadow ecosystem on the Tibetan Plateau. The decrease in $Q_{10}$ of $R_s$, as the warming amplitude rose may be attributed to the following mechanisms: (1) the soil inside the OTCs plots was dried by warming, which reduced the root and microbial activity, and (2) the substrate was limited and the temperature sensitivity of the soil enzyme decreased when it was exposed to a warm environment in a short period of time [19,28,43].

What’s more, the $R_s$ was low in the dry conditions because the soil drying could decrease the activity of the root and the soil microorganism and could inhibit its respiration via blocking the microbial to utilize the available substrate [50]. However, the soil CO₂ emission increased to a maximum at the intermediate moisture levels until it began to decrease when moisture content excluded oxygen [34,37]. A study showed that the soil moisture content together with the belowground biomass could account for 82% of the $R_s$ in an alpine grassland on the Tibetan Plateau [111]. Whereas, although the soil moisture content decreased by 11.8% – 20.5% at the 5cm depth and declined in different degree at the 20cm and 40cm depths in the warming treatment plots at our study site, the $R_s$ was much higher in the OTCs plots than that in the control plots during the study period (Figure 5). This was probably because the experimental warming caused the soil moisture content to reach the optimum water content [50] for the $R_s$ and as a result more oxygen was diffused into the soil, which accelerated the aerobic respiration of the soil microorganisms at the OTCs plots.

In addition, the experimental warming changed the freezing and thawing process of the active layer, prolonged the thawing period, and increased the thawed depth at our alpine meadow ecosystem site [47]. As a result, the microbial activities in the deep soil was activated [38,40] and the C assimilated by the canopy was consumed remarkably as the lower frozen soil thawed, which then increased the supply of carbohydrates to the below-ground microorganisms. So the $R_s$ of the alpine meadow ecosystem on the Tibetan Plateau would be accelerated by the long-term warming. The soil moisture decrease due to warming would be an important factor regulating the $R_s$ process in the alpine meadow ecosystem on the Tibetan Plateau. Nevertheless, much effort should be paid on revealing the mechanism of $R_s$ increasing as the soil moisture declined and on the threshold of the soil moisture regulating the $R_s$ of the alpine meadow ecosystem on the Tibetan Plateau. In addition, how to distinguish the root respiration and the
soil microbial respiration under different controlled soil moisture condition of the alpine meadow ecosystem on the Tibetan Plateau is still a difficult issue.

5. Conclusions

In our study, the daily mean nearsurface temperature increased by 6.33°C and 2.96°C, respectively, at the OTC2 and the OTC1 plots compared with that at the Control plots. The temperature increase amplitude at the OTC2 plots was higher than the warming increment (3.8°C) predicted by the IPCC on the Tibetan Plateau by the end of 21st century [17]. Our study clearly showed that the $R_s$ of the alpine meadow ecosystem on the Tibetan Plateau was rapidly responsive to the nearsurface warming. Experimental warming resulted in the increase of soil CO$_2$ emission rate by approximately 232% and 122% but the reduction of $Q_{10}$ by 3.72 and 3.33, respectively, under the condition of the two different warming magnitudes in the alpine meadow ecosystem. This result suggests that the sensitivity of response of the soil CO$_2$ emission to temperature increase would weaken as global warming continues.

However, it is still uncertain whether the carbon losses by $R_s$ would be offset by an increase of vegetation biomass for the alpine meadow ecosystem on the Tibetan Plateau. Thus, comprehensive studies, regarding photosynthetic carbon fixation, plant respiration, vegetation biomass dynamic and the distinction between root and microbial respiration, are needed to clarify the mechanism of carbon budget of the alpine meadow ecosystem in the scenario of global warming.

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References


ARTICLE

Paleo-environmental conditions, paleoclimatic significance and effects of weathering on clay deposits in the Lower Benue Trough, Nigeria. Mineralogical approach

A.T. Bolarinwa¹ S.O. Idakwo²* D.L. Bish³

1. Department of Geology, University of Ibadan, Ibadan, Nigeria
2. Department of Earth Sciences, Kogi State University, P.M.B. 1008, Anyigba, Kogi State, Nigeria
3. Department of Geological Sciences, Indiana University, Bloomington, Indiana, U.S.A.

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ABSTRACT

Combined methods for mineralogical identifications were used to characterise the clay deposits within the Lower Benue Trough of Nigeria to interpret paleo-environmental conditions, the paleoclimatic significance of the trough, and effects of weathering on the minerals as factors that favour its deposition/accumulation within the trough which host other important industrial minerals like coal, barite, limestone etc. Bulk-sample random-powder XRD data and data for clay fractions deposited onto zero-background quartz plates were measured. The samples contained kaolinite, vermiculite, and traces of smectite, and the non-clay phases included quartz, microcline, and muscovite. All samples were unaffected after glycolation, confirming the absence of significant smectite. Muscovite was characterized by the nature of its 10 Å basal peak with a width of <0.10° 2θ, which was very sharp. DTA/TGA results support the presence of kaolinite, and the characteristic kaolinite O-H, Al-OH, Si-OH and Si-O-Al FTIR bands also confirmed its presence. Vermicular and book-like morphologies were observed under the SEM, typical of kaolinitic clay from in situ alteration. High kaolinite abundance in these sediments is consistent with intense weathering of parent rocks rich in Al under wet/tropical paleo-climatic conditions with fresh and/or brackish water conditions in a continental setting. The variety of observed morphologies suggests that the deposits suffered more of chemical weathering. The clay deposits in Lower Benue Trough are quartz-rich, kaolinitic and derived from the chemical weathering of Al-rich source rocks.

1. Introduction

Clays are earthly and naturally fine-grained inorganic polymineralic materials of < 2 µm in size. The layered structures of these hydrated aluminosilicates clay minerals determine their characteristic chemical and physical properties of the clays which are formed as a result of chemical weathering of pre-existing crystalline rocks and feldspar minerals under warm tropical and subtropical climatic conditions or as a result of the hydrothermal alteration [1].

The basic structure of layer silicates and all silicates ion...
understand the change in mineral morphology associated with paleoclimate conditions from the clay assemblages and to interpret the paleoenvironment and subtle changes in conditions of the clay through the use of differential thermal analysis (DTA), thermogravimetry (TGA) and scanning electron microscope (SEM) were employed to understand significant compositional changes in response to biological, chemical and physical weathering [6,7]. It has been proven that imprints of the original composition of the precursor are readily preserved in the sediments [8,9,10].

In this present investigation, representative sedimentary clay samples from Mamu/Ajali and Enugu/Nkporo Formations within the Lower Benue Trough were examined mineralogically using combined methods: X-ray diffraction (XRD), differential thermal analysis (DTA), thermogravimetry (TGA) and scanning electron microscope (SEM) were employed to understand significant compositional changes in response to subtle changes in conditions of the clay through the use of DTA/TGA techniques, interpret the paleoenvironment and paleoclimate conditions from the clay assemblages and to understand the change in mineral morphology associated with weathering under different climatic conditions.

2. Location and geological description

The study area is located between latitude 6°00’ - 8°00’ N and longitude 6°50’ - 8°00’ E (Figure 1). The area is connected by tarred road, which leads from Alolo to Ofegijji, Udanebomi, Abocho, Agbenema, Eke-efe, Otukpa, Okpokwu and Enugu (Figure 2). The roads are motorable all the year round. Clay samples were collected from road cuts. Total area covered for this investigation is 25,134.84 km² (Figures 1 and 2).

Distributions of clay mineral of Cretaceous (Campanian-Maastrichtian) age in different geological situation that occurred in the Lower Benue Trough of Nigeria were studied (Figures 1 and 3).

Description of the unit starts with sedimentation in the Lower Benue Trough which commenced with the: Marine Albian Asu River Group, this constitutes the shales, limestones and lenses of sandstone within the Abakaliki Formation from the area of Abakaliki and the limestone of Mfamosing in the flank of Calabar [11] (Figures 4 and 5). Following this formation, Ezeaku Shales and the Makurdi Formation of Turonian occurred. The Ezeaku Shales is characterized with the presence of thick flaggy (calcareous and non-calcareous) shales, sandy and calcareous sandstones with shelly limestones. Outcrops of this formation are prominent towards the south area of Oturkpo division (Egedde-Oju area) with about 304.8 meters thick in the area and reaches 609.6 meters. Below the Ezeaku Formation is the marine Nkalagu Formation (black shales, limestones and siltstones) Cenomanian – Turonian. Deformation during the Mid-Santonian in the Benue Trough led to the displacement of the major depositional axis westward leading to the formation of the Anambra Basin. Therefore, Anambra Basin constitute the Post-deformational sedimentation in the Lower Benue Trough and sedimentation within the Anambra Basin commenced with the Campanian-Maastrichtian marine and paralic shales of the Enugu and Nkporo Formations, this is followed by the coal measures of the Mamu Formation. The Ajali and Owelli Formations is characterized by the presence of fluviodeltaic sandstones that lie conformably on the Mamu Formation and its lateral equivalents are constituted in most places. During the epoch of overall regression of the Nkporo cycle, coal-bearing Mamu Formation and the Ajali Sandstone accumulated. The Mamu Formation is characterized by a narrow strip trending north-south from the flank of Calabar, going west around the plateau of Ankpa and terminates close to River Niger at Idah [12] (Figures 4 and 5). During the Paleocene, another onset of transgression in the Anambra Basin was marked by the Nsukka Formation and the Imo shale while the regressive conditions was returned during Eocene by the mark of Nanka sands. These Nanka Formation gives an excellent opportunity to study deposits of tidal origin. Well-exposed, strongly assymetrical sandwaves suggest the predominance of flood-tidal currents over weak ebbreverse currents. The presence of the latter are only suggested by the bundling of lamine separated outcrop of the Nanka Formation is the Umunya section, 18km from the Niger bridge at Onitsha on the Enugu – Onitsha express-way (Figures 3,4 and 5).

Figure 1. The position of Lower Benue Trough within the map of Nigeria [12]
3. Materials and methods of study

Thirty four (34) clay samples representing different vertical sections of the exposures in Aloji, Agbenema, Ochipu, Otukpo, Okpokwu from Mamu/Ajali Formation and Enugu from Enugu/Nkporo Formation within the Lower Benue Trough were collected with effort made by avoiding weathered horizons (Figures 2, 3 and 6). The samples were pulverized and packaged for XRD, scanning electron microscope (SEM), differential thermal/thermo-gravimetric analysis (DTA/TGA), and fourier transform infra-red analysis (FTIR) at the Geological Sciences Department, Indiana University, Bloomington, Indiana, U.S.A.

Figure 2. Sample location on a sketch map of the study area

Figure 3. Location of exposures on the geologic map of Lower Benue Trough [13]

Figure 4. The N–S stratigraphic cross-section across the Benue Trough [12]

Figure 5. The Benue Trough: Its stratigraphic successions [14, 15]
X-ray diffraction analysis was performed using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (45 kV, 35 mA), step-scanning from 2°-70° and counting for 2 sec per 0.02° step. Data were analyzed using Bruker AXS Eva and Topas software. Both randomly oriented mounts and oriented mounts were carried out and the relative phase amounts (weight %) was estimated using the Rietveld refinement method \cite{16,17}.

In this work random orientation of the clay sample was achieved by allowing the free fall of the powdered raw clay samples into a 1 mm deep cavity in a Ti sample mount, thereby minimizing preferential orientation of clay crystallites while for the orient mount, the clay samples were prepared as follows: separation of fine fraction from the raw clay based on Stokes law settling in an aqueous. The method of separation involves placing a sample in the blender with distilled water, filling the blender about 1/3 full, and blending the sample for 10 minutes to dis-aggregate the material. All preparation steps to this point served to produce a disaggregated suspension of the material that is suitable for further size separation via settling and centrifuging. The content was poured into a beaker for sedimentation over about 24 hours. Turbid liquid in middle or upper was then poured into a centrifuge tube and centrifuge at 8000 r/min for 45 min. The residues in bottom of the tube was collected and spread on a glass dish for air dry. 5g of dried fine clay sample was then dispersed in distilled water for preparation of clay slurry. The clay slurry was sedimented onto a zero-background quartz plate to prepare an orient mount. The sample was dried on the quartz plate at room temperature and analyzed. The analyzed sample was exposed to ethylene glycol vapor for a minimum of 24 hours and then analyzed again.

The thermoanalytical methods complement the X-ray diffraction analysis (XRD). Thermal analysis (DTA/TGA) were carried out using a SDT 2960 Simultaneous DSC/TGA analyzer at a heating rate of 10°C/min in the range ambient to 900°C with alumina as standard. Size separated <2 µm samples were used for thermal analysis.

The morphology and texture of the clay particles were determined by scanning electron microscopy using an environmental SEM Scanning Electron Microscope (FEI Quanta 400 FEG) which requires no coating.

The fourier transform infra red (FITR) spectra of the samples were recorded between 4000 and 400 cm⁻¹ on Nicolet 6700 FITR spectroscope. The size separated < 2 m samples were dispersed in KBr in the ratio (1:200) and are pressed into discs at high pressure to obtain the transparent disc which was then placed in the sample compartment for scanning.

4. Results and Discussion

XRD data for clay samples from Lower Benue Trough, measured over the region from 2-70°, revealed two clay minerals (Figure 7). These include dominant kaolinite with peaks at 12.4°, 25° and 38° 2 – Theta, followed by traces of vermiculite with peak at at 6.1° 2 – Theta and non clay minerals include dominant quartz with peaks at 21°, 27°, 37°, 44°, 50° and 60° 2 - Theta while muscovite peaks were recorded at 8.9° and 17°, microcline occur at 27° and 30° 2 – Theta values correspondingly (Figure 7; Table 1). The clay samples are very similar in compositional trend. All the investigated clay samples were characterised by the presence of kaolinite, which constitute between 40-60 %, of all the clay and presence of high composition of quartz (50-69 %; Table 1) accounts for their grittiness. The presence of negligible peaks of microcline (1 – 5 %) and muscovite (1 – 8 %) in the raw clay samples (Figure 7; Table 1) suggests intense weathering of the parent rock to form the clay deposits. The presence of traces of vermiculite indicates alteration of biotite in the felsic protoliths to vermiculite.

**Figure 6.** Sample points of clay deposits

*Note: (A) at Aloji along Ayinba-Ito road, Mamu/Ajali Formation (7°24’45” N and 6°56’17” E) and (B) along the Abakaliki - Onitsha road, within Iva Valley, Enugu/Nkporo Formation (6°27’54.6’’ N and 7°27’17.1’’ E)\cite{13}.*

**Table 1**

<table>
<thead>
<tr>
<th>Clay Deposit</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>40-60%</td>
</tr>
<tr>
<td>Quartz</td>
<td>50-69%</td>
</tr>
<tr>
<td>Muscovite</td>
<td>1-8%</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>1-5%</td>
</tr>
</tbody>
</table>

DOI: https://doi.org/10.30564/jees.v1i2.904
XRD data were obtained for oriented aggregates over a 2θ range from 2° - 70° after the samples were (i) air dried and (ii) glycolated. Data for air-dried samples revealed the presence of kaolinite at 12.4°, 25° and 38° 2θ and traces of vermiculite at 20 value of 6.1° (Figure 8; Table 2). Quartz peaks are mostly at 21°, 27°, 37°, 44°, 50° and 60° 2θ values while muscovite occur at 8.9° and 17°, microcline at 27° and 30° 2θ values (Figure 8; Table 2). All the investigated air-dried samples contained abundant kaolinite (39 -79 %) but poor in quartz (17 – 40 %) compared to the raw clay samples with kaolinite of 40 – 60 %, quartz 50 -69 %.

Muscovite, a 2:1, dioctahedral mica, was observed at 8.9° to 17° 2 - Theta. Illite and muscovite were distinguished using the method that starts that very sharp 1st order basal peak with a width of <0.10° 2θ is related to muscovite and broad peaks to Illite [18, 19] (Figure 8). The presence of muscovite (1 – 8 %) and traces of microcline (1 – 7 %) suggest felsic source rock that suffered incipient weathering and moderate distance of transportation (Table 2). The mineralogy of the solvated, ethylene glycol treated clay samples showed that the kaolinite peaks at 12.4°, 25° and 38° 2θ values, in all samples, were not affected (Figure 8). Vermiculite also showed no shift in the 6.1 2θ peak (Figure 8). The observed feldspar and muscovite peaks

![Figure 7. X-ray diffractogram of raw clay sample from Aloji (AL1.1), Oturkpa (OT1.1) and Enugu (EN4.3) within the Lower Benue Trough, Nigeria K - Kaolinite, M - Muscovite, Q - Quartz](image)

**Table 1.** Mineralogical composition (% vol.) of raw clay deposits from different locations within the Lower Benue Trough, Nigeria

<table>
<thead>
<tr>
<th>Sample No → Mineral</th>
<th>AL1.1</th>
<th>AL1.2</th>
<th>AL1.3</th>
<th>AL2.1</th>
<th>AL2.2</th>
<th>AL2.4</th>
<th>AL2.5</th>
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</tbody>
</table>

Mamu/Ajali Formation clay:
Aloji samples
AL1.1, AL1.2, AL1.3, AL2.1, AL.2.2, AL. 2.4 and AL2.5.
Ofejiji samples
OF1.1, OF1.3, OF2.1, OF2.2, OF2.3, OF2.4 and OF2.5.
Agbenema samples
AG1.1, AG1.2, AG2.1 and AG2.2.
Oturkpa samples
OT1.1 and OT1.2, OT2.1, OT2.2.
in raw and air dried samples were retained in the treated samples (Figure 8).

Data obtained from the raw clay samples of Aloji, Ofejiji, Agbenema, Oturkpa, Okpokwu and Enugu of Mamu/Ajali and Enugu/Nkporo Formations shows that the clay deposits are kaolinitic with appreciable amounts of microcline and muscovite and very high quartz content. The presence of kaolinite, quartz and muscovite suggests derivation of the clays from felsic rocks in a continental environment.

Table 1. Cont.

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<th>Sample No → Elements</th>
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<th>OK3.2</th>
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</table>

Mamu/Ajali Formation clay samples:
Okpokwu - OK 1.1, OK1.2, OK 3.1 and OK3.2.

Enugu/Nkporo Formation clay samples:
Enugu - EN2.1, EN2.2, EN3.1, EN3.2, EN4.1, EN4.2 and EN4.3.
Okpokwu - OK 1.1, OK1.2, OK 3.1 and OK3.2.
Enugu/Nkporo Formation clay samples:
Enugu - EN2.1, EN2.2, EN3.1, EN3.2, EN4.1, EN4.2 and EN4.3.

Table 2. Mineralogical composition (% vol.) of <2μm clay fractions from Mamu/Ajali and Enugu/Nkporo Formation within the Lower Benue Trough, Nigeria

<table>
<thead>
<tr>
<th>Sample No → Minerals</th>
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<th>AL1.3</th>
<th>AL2.1</th>
<th>AL2.2</th>
<th>AL2.3</th>
<th>OF2.1</th>
<th>OF2.2</th>
<th>OF2.3</th>
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<td>Kaolinite</td>
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</tbody>
</table>

Mamu/Ajali Formation clay samples:
Aloji - AL1.1, AL1.2, AL1.3, AL2.1, AL2.1 and AL2.3.
Ofejiji - OF2.1, OF2.2 and OF 2.3.
Agbenema - AG1.1, AG1.2, AG2.1 and AG2.2.
Oturkpa - OT1.1, OT1.2, OT2.1 and OT2.2.
Okpokwu - OK1.1, OK1.2, OK3.1 and OK3.2.
Enugu/Nkporo Formation clay samples:
Enugu - EN2.1, EN2.2, EN3.1, EN3.2, EN4.1, EN4.2 and EN4.3.
Figure 8. X-ray diffractogram of glycolated <2 µm clay samples from Aloji (AL1.1), Oturkpa

Note: (OK2.2) of Mamu/Ajali Formation and Enugu (EN4.2) within the Lower Benue Trough, Nigeria. V - Vermiculite, M - Muscovite, K - Kaolinite, Q - Quartz

The thermal properties of the investigated clay were undertaken using differential thermal and thermogravimetric analysis (DTA and TGA). The characteristic patterns of the fine fractions (< 2 m) and loss in volume is presented in Figures 19 to 21 and Table 2 accordingly. DTA and TGA curves of the clay samples are given for the temperature range of 10-900°C. The first endothermic peak observed within the range of 138 – 154°C is due to the elimination of hygroscopic and zeolitic waters; the second endothermic peak observed within the range of 408.41 to 519.67°C is due to dehydroxylation [20, 21]. The last endothermic peak between 860 to 900°C is followed by an exothermic peak due to recrystallization into a possible new phase formation known as mullite [21].

The weight loss during thermogravimetric analysis revealed that samples from Mamu/Ajali Formation ranged between 0.76 to 1.26 mg (Figure 9a and Table 3) while those of Enugu/Nkporo Formation is 1.21 to 2.11 mg (Figure 9b and Table 3). The slightly higher values of the Enugu/Nkporo Formation samples could be attributed to presence of higher finer particles with organic matter. Weight loss for all the clay samples were recorded between 499 °C and 504 °C, probably due to large organic matter decomposition with loss in weight increasing with temperature. This is consistent with author 21 assertion that kaolinites undergoes dehydroxylation at 408°C to 520°C to form metakaolin. The thermogravimetric patterns (Figures 9a – c; Table 3) of the fine (<2µm) clay sample is generally consistent with the results of the mineralogy.
were subjected to IR spectral studies. The characteristic infrared spectra of the sampled clay is presented in Figures 10 a – c and Table 4 revealed Al – O – H stretching at 3659.51 cm\(^{-1}\) to 3696.20 cm\(^{-1}\) bands, typical of kaolin group, 3621.22 cm\(^{-1}\) and 3622.12 cm\(^{-1}\) infers OH stretching and bands between 3438.28 cm\(^{-1}\) and 3447.25 cm\(^{-1}\) reflects absorption of water (H – O – H) within the crystal layers of the clay mineral, but this was absent in one sample from Aloji (AL1.1), this suggest presence of high quartz (Figure 10a). A C – H stretching occurred at 2925.97 cm\(^{-1}\) in one sample from Enugu (EN3.1) (Figure 20c, Table 4), inferring presence of organic matters. Bands ranging from 1625.47 cm\(^{-1}\) – 1628.25 cm\(^{-1}\) observed in all the investigated samples except for two samples from Aloji (AL1.1 and AL1.2) describes the presence of water (H – O – H bending of water), another, typical spectrum kaolin was observed within the range from 1104.00 cm\(^{-1}\) to 1110.08 cm\(^{-1}\) with an AL – O – H stretching characteristic. From 915.12 cm\(^{-1}\) to 918.10 cm\(^{-1}\), which is close to the proposed value of 912 cm\(^{-1}\) reflects OH – deformation linked to th 2Al\(^{2+}\) while the bands varying from 689.76 cm\(^{-1}\) to 790.41 cm\(^{-1}\) reflects abundance of quartz (Figure 10 a – c; Table 4.4). The bands between 538.17 cm\(^{-1}\) and 542.45 cm\(^{-1}\) close to the proposed 537 cm\(^{-1}\) reveals the presence of Fe\(^{2+}\) and Si – O – Al stretching but 457.24 to 471.11 cm\(^{-1}\) spectrum bands signify Si – O – Si bending.

Si-O and Al-OH functional groups are in the 1000 cm\(^{-1}\) and 500 cm\(^{-1}\) region. Muscovite and possibly quartz interference was observed at 1032.16 in Oturkpa (OT2.2), 1034.21 in Okpokwu (OK1.1), 1030.06 and 1033.52 in Enugu (EN3.1 and EN4.2) for the studied clay samples. The corresponding bands at 915.78 – 918.17 cm\(^{-1}\) infer Al-OH bending vibrations but 784.76 - 789.78 cm\(^{-1}\) suggest Si-O-Si inter tetrahedral bridging bonds in SiO\(_2\) for typical kaolinitic clay minerals. The bands between 1625.94 – 1888.91 cm\(^{-1}\) signifies the region were OH deformation of water is found (Table 4). The FTIR results corroborated the quartz-rich, kaolinitic clay results obtained from the XRD data of the clay deposits.

The obtained FTIR bands of the clay samples were compared with a proposed typical kaolinitic spectrum\(^{22}\) as shown in table 4.
Scanning electron micrographs were obtained for sample Aloji (AL1.1), Oturkpa (OT2.2) from Mamu/Ajali Formation, Enugu (EN4.2 and EN4.3) from Enugu/Nkporo Formation within the Lower Benue Trough. Fine (<2µm) clay samples were used for the SEM analysis. The micrographs provided the informations on the physical, geochemical processes and the environment in the genesis of the sedimentary clays.

The vermicular and book-like morphological characteristic under the SEM (Figures 11a, b, c and d), suggest a typical kaolinitic feature for the clays under investigation, generated from weathering processes [23, 24]. A face-to-face pattern of arrangement of platy crystals was observed in all the analyzed samples, this infers grains of kaolinite (Figure 11a). The irregular angular kaolinite edge is characteristic of actively growing crystals [23]. A swirl-like texture of muscovite was observed more in samples from Otukpa (OT2.2), and Enugu (Figure 11c) in association with face-to-face arrangement of kaolinitic grains and vermiculite, suggesting their detrital origin [24].

Table 4. Wavenumbers of clay samples from Mamu/Ajali and Enugu/Nkporo Formations from Lower Benue Trough compared to theoretical kaolin

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<tr>
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<th>AL1.3</th>
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<th>EN 2.1</th>
<th>EN 4.3</th>
<th>EN 4.2</th>
<th>EN 3.1</th>
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Mamu/Ajali Formation samples:
- Aloji – AL1.1, AL1.2, AL1.3
- Eke-efe – EK1.2, OK1.1, OT2.2.

Enugu/Nkporo Formation samples:
- Enugu – EN3.1, EN4.2, EN4.3

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imentary clay, finer clay grains are agglomerated as they are deposited by the cementing effect of organic matter thereby giving a flower - like appearance (Figure 11b). Two types of grains were observed, infering the diversity of the environment for their formation. Smaller kaolinite grains surround larger grains of smooth edges (Figure 11b). These bimodal features indicate that the finer grains are recrystallized product while the coarser grains are of detrital origin. Such a texture in kaolinite occurs due to incipient formation of this particular mineral in a waterlaiden condition from silicate parent material [23] (Figure 11 d).

The clay morphology reflected varied characteristic shapes in different environment of deposition within the Lower Benue Trough. A characterised thin plates and embayed edge was observed in all the clay samples (Figures 11c and d), suggesting that the clay underwent relatively stronger chemical weathering than physical weathering.

This study have proven that there is no evidence of the role of diagenesis in the formation of the clay minerals in the study area because there no observed change in the morphology of kaolinitic clay from aggregates of books to individual blockier crystals and on that basis, it can be an important tool in paleoclimatic studies [25] (Figures 11 a, b, c and d).

Note: A = Aloji (Al.1.1), showing vermicular and book- like kaolinites having thin plates and embayed edge in association with detrital muscovite and B = Oturkpa (OT2.2) showing shaggy appearance of kaolinite books with thin plates within muscovite matrix showing flower/swirl – like structures.

Figure 11 a, b. Scanning electron micrographs of clay samples from Mamu/Ajali Formation, Lower Benue Trough, Nigeria

Figure 11 c, d. Scanning electron micrographs of clay sample from Enugu/Nkporo Formation, Lower Benue Trough

Note: (C) EN4.2 showing the smaller grains of kaolinite grains surrounding larger muscovite grains and (D) EN4.3 Muscovite surrounded by grains of kaolinite.

4.1 Paleo-environmental Conditions

The XRD, TGA/DTA, FT-IR and SEM result confirms that the clay deposits in Aloji, Ofejii, Udane-Biomi, Agbenema, Oturkpa, Okpokwu from Mamu/Ajali Formation and Enugu from Enugu/Nkporo Formation are largely dominated by kaolinites with traces of vermiculite. This reveals that both formations are characterised by high compositional value of kaolinitic clay mineral from continental marginal setting compared to clay types like illite and smectite of marine marginal setting. It is also known that kaolinite concentration is more in sediments close to the shore compared illites and smectites that increases in composition with distance from the shoreline [26].

Base on the dominant kaolinitic clay mineral which was probably derived from weathered crystalline rocks...
containing K-feldspar (microcline) and muscovite, suggestive of the basement rocks surrounding the trough, such as the Eastern Nigeria, North central Nigeria and the Oban Massif \(^{12}\) a continental environment can be envisaged as probable depositional environment for the two formations.

### 4.2 Paleoclimatic Significance

Clay minerals are significant tool widely used in interpreting, understanding and solving problems such as tectonics, source rock, zonation, age, metamorphism, oil exploration and its latest application is in the area of paleoclimatic studies. It is worthy of note that climate major controlling factor over the clay type that can be formed at a particular point in time in a given location; base on this, clay minerals can be a powerful tool in paleoclimatic studies inorder to recognize warm and humid climatic condition typical for the formation of kaolinitic clay minerals, or dry seasons, for illite or smectite formation because these two-layer/three-layer ratios of clay minerals, or dry seasons, for illite or smectite formation are conditioned by climate. Based on the dominant clay mineral recorded, it can be concluded that the Clay mineral assemblage from Ajali/Mamu and Enugu/Nkporo Formations within the Lower Benue Trough have being used to elucidate the paleo-environmental conditions, paleoclimatic significance and effect of weathering during their formations.

Mineralogical analysis using XRD, DTA/TGA, FTIR and SEM methods of analysis revealed that the bulk mineral composition of the clay samples are kaolinite and vermiculite as the mineral phase and microcline, muscovite and quartz as non clay phases. The dominant clay minerals kaolinites with traces of vermiculite; suggested to be a result of some controlling factors like source rock, climatic conditions, size sorting and environment of deposition. The dominance of kaolinites suggests that the clays are deposited in an environment that correspond to continental setting, its dominance also reflects that they must have being subjected to strong chemical weathering with very good leaching, favoured by tropical to sub-tropical humid climates as observed morphologically under the SEM. This evaluation has proven that despite that both formations are in different stratigraphic locations, they were both deposited relatively under similar conditions of climate and environment. Therefore, the clay deposits in the Lower Benue Trough are quartz-

### 4.3 Weathering Effect

The observed clay morphology varied remarkably in shape from one depositional environment to another. Some of the clays occurred as thin plates with embayed edge, suggesting the clay underwent relative stronger chemical weathering and displayed thicker plates indicates a condition of dominative physical weathering. These characteristics suggest that the clay underwent to some extent chemical weathering. These shape changes reflected the changing weathering conditions, and suggested that climate played an important role in these variation of mineral morphology with the gross genetic environment during formation of the clay. Controlling environmental factors for kaolinization include parent material and concentration of ions in the fluids of kaolinization \(^{24}\). SEM observations show that the clay deposits of the Lower Benue Trough consist of many stacks or books of kaolinite flakes, a typical feature of kaolinite generated from the process of weathering \(^{22, 23}\) (Figures 11 a, b, c and d).

High content of quartz observed in the raw clay samples (Table 1) must be as a result of renewed tectonic activity within the Lower Benue Trough during the mid Santonia when there was a displacement of the major depositional axis westward \(^{12}\) which disturbs the sedimentation dynamics, possibly resulting in sediment mixing and reworking.

### 5. Conclusion

Clay mineral assemblage from Ajali/Mamu and Enugu/Nkporo Formations within the Lower Benue Trough have being used to elucidate the paleo-environmental conditions, paleoclimatic significance and effect of weathering during their formations.

High content of quartz observed in the raw clay samples (Table 1) must be as a result of renewed tectonic activity within the Lower Benue Trough during the mid Santonia when there was a displacement of the major depositional axis westward \(^{12}\) which disturbs the sedimentation dynamics, possibly resulting in sediment mixing and reworking.

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rich and kaolinitic in nature derived from the chemical weathering of Al-rich source rocks under wet/tropical paleo-climatic conditions with fresh and/or brackish water conditions in a continental setting.

Reference


ARTICLE

Are Environmental Vanguard Firms More Proactive Towards Environmental Conservation? An Empirical Study of Power Sector Firms in India

Arun Kumar Vishwakarma1* Arvind K Nema2
1. National Institute of Industrial Engineering, Mumbai, India
2. Indian Institute of Technology Delhi, New Delhi, India

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ABSTRACT

Environmental protection is a crucial issue for environmentalists and researchers. Almost every stakeholder in the industrial production process of a product is concerned about the detrimental effects on the environment due to emissions. Though environmental regulations are in place, some firms across diverse industrial sectors are considered as the environmental vanguard, i.e., leaders in environmental protection. Does being environmental vanguard result in environmental proactivity? This paper, through an empirical study of Indian power sector firms, studies the environmental proactivity of the firms who are known to be leaders in the adoption of environmental protection norms. A questionnaire-based survey method is used to analyse the responses statistically. The study uses 280 responses for the analysis of the data. Eight hypotheses are proposed and tested statistically through Structural Equation Modelling (SEM). The statistical analysis reveals that the firms who are environmental vanguard are more proactive towards environmental protection. The findings of the study can be useful for the policymakers and environmental managers in the formulation of policies which can be considered as a benchmark for the firms for the protection of the environment.

1. Introduction

This paper analyses empirically the proactive environmental behaviour of environmental vanguard firms having their operations in emission intensive areas. Growing number of firms are concerned towards sustainability.

These companies target their operations to reduce their impact on the environment and are in the process of envisaging new techniques to derive greater environmental advantages [1, 2]. Firms adopt environmental management system which provides “plan, do check, act” model guidelines to improve their environmental performance considering their manufacturing activities [3, 4, 5]. This change in perspective of the firms towards environmental damage has created an interesting field of study for the researchers. There may be various reasons which involve concern towards the emissions from the manufacturing process; firms’ reputation, proactive corporate policy, product and brand differentiation, innovation, customers concern and cost savings and liability reduction [6, 7]. According to a study environmental innovations can be defined as “......
measures of relevant actors (firms, private households), which: (1) develop new ideas, behaviour, products and processes, apply or introduce them, and (2) contribute to a reduction of environmental burdens or to ecologically specified sustainability targets\textsuperscript{8}. Apart from environmental innovations, a distinction can be made towards product and process innovations\textsuperscript{9,10,11}. A study mention, that by minimising their emissions and waste, firms can benefit from their operations, which includes cost savings, higher productivity, and innovation\textsuperscript{12}. The firms in the U.S. have substantially increased their expenditure to further expected increase in future\textsuperscript{13}. Considering the quantum of expenditure required towards environmental protection since the 1970s with the further expected increase in future\textsuperscript{13}. The responsibility of the identification of waste reduction prospects was for the first time handed over to line workers and employees in place of environmental engineers and legal experts\textsuperscript{18}. Environmentalists like\textsuperscript{16, 19} and many others\textsuperscript{20, 21, 22} endorsed the view of the companies following the 3M model. Control or prevention can reduce emission. Different strategies are adopted to reduce emission through either of the two options\textsuperscript{21, 23, 24}.

Several studies, mention efforts made by few companies to achieve better corporate environmental management and gain competitive advantage by adopting environmental strategies and using environmental management accounting\textsuperscript{25, 26}. The commitment of top managers of environmental vanguard firms helps in achieving an enhanced competitive advantage\textsuperscript{16, 27}.

Many researchers have contributed to the field of factors governing the environmental proactiveness of firms throughout the globe. However, very few studies are available which contribute to such studies of Indian firms. The Indian power sector has grown tremendously over the decades. Thermal power has a majority share of total power generation. Thermal power generation primarily uses coal. The technical and commercial losses in the power sector were one of the highest in India. Incorporation of better technologies has helped in reducing losses. The power sector in India, which was a state dominated sector, was opened up for private firms in the early 1990s. Competition ensured advanced technologies to make better use of input fuels and to increase the output. Pressure from the regulatory authority forced the firms to adopt environmentally friendly measures. Through innovative ideas, power sector firms can offer competitive tariffs and thus increasing their market share. By reducing the losses, they can gain a competitive advantage. Prior assessment of environmental legislation helps in better preparedness for the more stringent future environmental norms. The firms are not hesitant in adopting an effective approach to identify future environmental liabilities and the ability to tackle them without cost consideration.

The outcome of the earlier studies are helpful, but they cannot be generalised for countries like India. The study intends to find whether the power sector firms in India who are environmental vanguard are environmentally proactive or not. The study is based on a questionnaire based survey. Exploratory Factor Analysis (EFA) and Confirmatory Factor Analysis (CFA) are used to identify the relationship between the variables. Eight hypotheses are proposed and statistically tested using SEM.

2. Research Question

In spite of applicable environmental regulations, some firms are more inclined towards environmental protection. What are the reasons for such environmental proactiveness? Factors are identified through a literature review, questionnaire survey, and experts’ opinion. The study intends to test the hypotheses proposed based on factors identified statistically. The study aims to understand whether the power sector firms in India who are environmental vanguard are environmentally proactive or not.

3. Literature Review and Hypotheses Development

3.1 Proactive Environmental Strategies

Various researchers have proposed multiple definitions of proactive environmental strategies (PES). It is an accepted fact that the general level of strategic proactiveness of a firm is related to its environmental strategic proactiveness\textsuperscript{28, 29}. PES are mentioned as strategies which are beyond compliance but are different from over compliance\textsuperscript{30}. In the over-compliance, the firms seek to follow government regulation but deliver more than the legal requirement due to technological indivisibilities. Therefore, beyond compliance policies deliberately intend to deliver more than...
the requirement of existing laws. Several researchers have mentioned environmental strategies which can be classified as PES. “Role of the characteristics of the firm to explain the adoption of ‘beyond compliance’ strategies” has been looked at by other researchers, including “the influence of organisational context and design” [20, 31, 32, 33] along with “organisational learning” [34]. Focus on the “individual or managerial level,” analysing the “role of leadership values” [35], and “managerial attitudes” [32] are mentioned. However, there is still more to be understood about the conditions which explain the PES adoption beyond legal compliance at the plant level [36].

3.2 Research Hypotheses

This paper investigates the factors which are responsible for the adoption of PES by the power sector companies in India. Based on the literature review, the following factors are considered to be primarily responsible for PES adoption:

**Innovation**

Technological innovation is an essential requirement for sustainable development. After initial 1990s, the initiation of globalisation and start of increased awareness towards sustainable development, industrial environmentalism was accepted as a tactic for improving the environmental effectiveness of the technological systems [37]. According to [38], environmental impact can be explained by the equation:

\[ I = P \times A \times T \]

where,

- \( I \) = environmental impact
- \( P \) = population
- \( A \) = affluence (consumption of services and products per capita)
- \( T \) = technology (environmental burden per product or service unit)

As population and affluence are the social and political issues, technology remains the only alternative to minimise the environmental impact.

From the above discussion, the following hypothesis (H) can be derived:

**Hypothesis 1 (H1): Innovation is positively associated with the adoption of PES.**

**Environmental stewardship**

Environmental stewardship assimilates three largely interconnected sustainability approaches [39, 40, 41]. These approaches are: (i) minimising vulnerability to anticipated changes [40, 42], (ii) developing flexibility to withstand expected circumstances in the event of unrests and uncertainty [43], and getting prepared to overcome from adverse situations to take on emerging opportunities [44]. Environmental stewardship involves trade-offs between efficiency and resilience along with near and long-term benefits [3, 45]. According to [46], product stewardship aims to not only minimise pollution during the manufacturing process but also all the adverse environmental impacts during the product life cycle. Based on the above arguments following hypothesis is proposed:

**Hypothesis 2 (H2): Sincere environmental stewardship is positively associated with the adoption of PES.**

**Defined environmental policy**

The regulatory authority offers possible control relief for environmental front runners on various levels. This relief from the regulatory authority was claimed as a possible benefit for firms, and subsequently, it became a practice for firms investing in environmental systems which are compliant to Eco-Management and Audit Scheme (EMAS) and ISO 14000 [47]. It may be an interesting finding for the regulatory bodies after years of experience to know whether if such practices are worthwhile, i.e., firms having a defined environmental policy are performing better than those without defined environmental policy. It is an interesting motive to analyse whether environmental performance is improved by the Environmental Management System (EMS), and enhanced environmental performance becomes a benchmark [48].

The above discussion gives rise to the following hypothesis:

**Hypothesis 3 (H3): Defined environmental policy is positively associated with the adoption of PES.**

**Effective approach to identify future environmental liabilities**

In the 1990s, the firms started adopting proactive environmental management strategies, through which they initiated anticipation of adverse environmental impact of their operations, started measures to reduce pollution and waste prior to regulation, and evolved optimistic approach of taking benefit of business opportunities by adopting total quality environmental management [49]. Many firms integrated values in their corporate cultures and management processes. A “second bottom line” has emerged as auditing and accounting practice for environmental impacts in an increasing number of firms [50]. Even though environmental impacts may not be quantified financially, companies cannot afford to ignore them [51]. Above discussion leads to the following hypothesis:

**Hypothesis 4 (H4): Effective approach to identify future environmental liabilities and the ability to tackle them without cost consideration is positively associated with the adoption of PES.**
Product and brand differentiation

Difficulty in the differentiation of products or services based on noticeable quality features can be overcome through the brand image [52]. Considering the increased consumers’ environmental consciousness and stringent environmental regulations, the green brand image of the company plays a crucial role. Companies can reflect the low carbon footprint of their product to achieve product differentiation [16, 33, 54]. As a better brand or green image may not only avoid business disruption, environmental protests, and penalties but also helps the firms to increase their customers’ satisfaction about environmental concerns. The power sector companies can build a product and brand differentiation by ensuring that the majority of their generation is from the renewable sources of energy, thus minimising emissions. Based on the above discussion following hypothesis is proposed:

Hypothesis 5 (H5): Product and brand differentiation are positively associated with the adoption of PES.

Prior assessment of future environmental legislation

Prior assessment of future environmental legislation helps the companies to take corrective action by reducing waste and pollution, preventing regulatory enforcement [56]. This helps them in getting market benefits as compared to competitors who fail to anticipate future regulations. Expertise available towards “renewable energy technologies, carbon capture and storage and highly efficient fossil fuel power plants” can be a key lever for achieving emission cut target [55]. It is a general belief that pollution prevention pays. The proactive firms (lower polluting) may be adopting more advanced strategies build on low emissions involving other sources of sustainable competitive advantage [56]. The proposed hypothesis is based on the above discussion:

Hypothesis 6 (H6): Prior assessment of future environmental legislation is positively associated with the adoption of PES.

Customer concern for the environment

Several studies reason why firms act voluntarily to improve their environmental performance beyond the requirement of extant laws. Considering the firm as a rational actor, the economists suggest that firms believe such voluntary action will help them to market their product by influencing the customers, asking high price considering the customer concern for the environment, and creation of a market for products with low carbon footprints [37]. Customers, investors and other stakeholders can influence a firm’s behaviour through products and capital markets. Companies may adopt PES through reasonable efforts by improving their environmental performance and addressing the concerns of customers and stakeholders [59]. Above discussion leads to the following hypothesis:

Hypothesis 7 (H7): Customer concern for the environment is positively associated with the adoption of PES.

Cost saving and liability reduction

[59] identified that implementation of supply chain management practices could result in reduced inventory level, reduced lead time in production, increased flexibility, accurate forecasting, cost saving and accurate resource planning. Whereas, companies who implement green supply chain management practices gain due to cost savings (effective raw material utilisation, reduced energy and water use), improved public image and reduced environmental liability [50]. Poor environmental accomplishment can result in significant ecological damage resulting in monetary cost for the companies. [61] mention companies’ pro-environmental behaviour is closely associated with its financial performance. Firms which are sensitive towards the environment can generate the confidence of the regulators and investors. Above discussion leads to the following hypothesis:

Hypothesis 8 (H8): Cost saving and liability reduction are positively associated with the adoption of PES.

3.3 Hypothesised Model

Figure 1 shows the hypothesised model.

4. Research Significance and Objectives

Primarily the study intends to deliver information and evidence based understanding regarding the environmental proactiveness of environmental vanguard firms in the Indian power sector. Although there are many studies available on proactive environmental strategies, however, only a few of them are sector specific. The study attempts to identify the reasons for the environmental proactiveness in Indian power sector firms. The variables selected are beyond the purview of the regulatory authority. The study will help the policymakers of the environmental manage-
5. Research Design and Methodology

5.1 Sample and data collection

The study uses primary as well as secondary sources of information. The questionnaire, focus group study and interviews formed the basis of primary data collection. The annual reports published by the companies contributed to the secondary data. Two focus group studies helped in understanding the key dimensions of the study. Two interviews 45-60 minutes duration were conducted. The period of the study was from May-2015 to July-2016. The interviews, literature available along with focus group study helped in designing a questionnaire which was related to work done in similar areas [14, 29, 30].

The study adopts survey method which helps in collecting a large number of responses in a short period. The questionnaire method of data collection offers certain benefits, which are inexpensive and offer quick results. Considering these benefits, both mail and self-administered questionnaires are used as an instrument for data collection. The target population for the study are the power sector firms in India who ensured regular environmental or sustainability reporting. The study followed a modified scale development methodology of [62] used by [63, 64, 65] where EFA and CFA were conducted on the total sample size. For the initial EFA, a total of 90 responses were used to assess initial reliability. For further validation, 190 responses were collected additionally for the analysis. Finally, the EFA and CFA were performed on a total sample size of 280 [65]. The study adopts a non-probabilistic sampling strategy combined with snowball sampling method to select the firms for the study. Snowball sampling involves requesting a respondent to suggest another similar respondent [66].

Out of total 280 level wise respondents, 63 respondents were from the junior level of the management comprising 22.50%, 110 from the middle level comprising 39.28% and 107 from the senior level comprising 38.22%. Department wise out of total 280 respondents, 123 respondents were from the environment department comprising 43.93%, 80 from the maintenance department comprising 28.57%, 62 from the finance department comprising 22.14%, and 15 from the others comprising 5.36%.

5.2 Questionnaire Design

The questionnaire method was preferred because it permits collecting a relatively large sample in a short period. The pilot study validated the pre-tested questionnaire. Based on the pilot study, the final questionnaire was prepared, which included a covering letter mentioning the purpose of the study with anonymity assurance to the respondents. The first part of the questionnaire covered the necessary information of the respondents like name, department, designation, and sector, along with a brief introduction to the research. While the second part consisted of various items capturing the essence of different constructs like innovation, environmental stewardship, defined environmental policy, effective approach to identify future environmental liabilities and ability to tackle them without cost consideration, product and brand differentiation, prior assessment of future environmental legislation, customer concern for environment, and cost saving and liability reduction. The final questionnaire used for the survey consisted of eight items. These eight questions were marked as EVO 1 to EVO 8. All the measurements in the study are subjective assessments by the respondents using a seven-point Likert scale ranging from 1= Strongly Disagree to 7= Strongly Agree.

5.3 Data Analysis

Statistical Package for Social Sciences (SPSS) version 23 is used for the quantitative analysis of data. The coefficient of α, i.e. (Cronbach’s α), is a coefficient that indicates inter-correlation among the items. In other words, it determines the extent of measures in capturing a particular concept. The coefficient of α determines the statistical significance of survey measures. The value of the coefficient of α ranges from 0 to 1. The measure is considered statistically significant if the Cronbach’s α value is closer to 1. This means that items which measure a particular concept are highly correlated with each other. Therefore, the reliability of a measure is confirmed by calculating Cronbach’s α. For the current study, the value obtained is 0.949, indicating reliability and validity of the scale. Table 1 shows the reliability analysis.

<table>
<thead>
<tr>
<th>Reliability Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cronbach’s Alpha</td>
</tr>
<tr>
<td>Based on Standardised Items</td>
</tr>
<tr>
<td>.949</td>
</tr>
</tbody>
</table>

Table 1. Reliability analysis
Suitability of data for factor analysis is measured by the Kaiser-Meyer-Olkin (KMO) Test. The sampling adequacy for individual variable and the complete model is measured by this test. KMO must be > 0.60 for good factor analysis \[67\]. All analysis for the present study was done at a 95% confidence interval. The KMO value obtained is 0.920 at a significance level of 0.000, which indicates the suitability of data for factor analysis.

Table 2 represents the outcome of KMO analysis.

Table 2. KMO Analysis

| Kaiser-Meyer-Olkin Measure of Sampling Adequacy: | .920 |
| Bartlett’s Test of Sphericity | |
| Approx. Chi-Square | 2474.998 |
| df | 28 |
| Sig. | .000 |

Latent variables identification through factor analysis contributes to a common variance in a measured variables set. Two factors emerge having Eigen value >1. These two factors represent the variance of 87% out of the total variance. Table 3 represents the variance of items. Extracted and rotated sum of squared loadings are also shown in the table.

Table 3. Total variance explained (Extraction method: Principal Component Analysis)

<table>
<thead>
<tr>
<th>Component</th>
<th>Initial Eigenvalues</th>
<th>Extraction Sums of Squared Loadings</th>
<th>Rotation Sums of Squared Loadings</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>% of Variance</td>
<td>Cumulative %</td>
</tr>
<tr>
<td>1</td>
<td>5.920</td>
<td>74.002</td>
<td>74.002</td>
</tr>
<tr>
<td>3</td>
<td>.245</td>
<td>.902</td>
<td>90.283</td>
</tr>
<tr>
<td>4</td>
<td>.198</td>
<td>.87</td>
<td>92.760</td>
</tr>
<tr>
<td>5</td>
<td>.181</td>
<td>95.019</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>.156</td>
<td>96.970</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.128</td>
<td>98.565</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>.115</td>
<td>100.000</td>
<td></td>
</tr>
</tbody>
</table>

Descriptive analysis showing minimum, maximum, mean, standard deviation and variance is shown in Table 4.

Table 4. Descriptive Statistics

<table>
<thead>
<tr>
<th>Statistic</th>
<th>N</th>
<th>Range</th>
<th>Min-</th>
<th>Maximum</th>
<th>Mean</th>
<th>Std. De-</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Statistic</td>
<td>Statistic</td>
<td>Statistic</td>
<td>Statistic</td>
<td>Statistic</td>
<td>Std. Error</td>
<td>Statistic</td>
<td>Statistic</td>
</tr>
<tr>
<td>EVO1</td>
<td>280</td>
<td>6</td>
<td>1</td>
<td>7</td>
<td>4.29</td>
<td>.123</td>
<td>2.065</td>
</tr>
<tr>
<td>EVO2</td>
<td>280</td>
<td>6</td>
<td>1</td>
<td>7</td>
<td>4.24</td>
<td>.112</td>
<td>1.870</td>
</tr>
<tr>
<td>EVO3</td>
<td>280</td>
<td>6</td>
<td>1</td>
<td>7</td>
<td>4.58</td>
<td>.118</td>
<td>1.968</td>
</tr>
</tbody>
</table>

Table 5 shows the factor loadings, % variance explained and Eigen value of the two factors.

Table 5. Factor Loadings

<table>
<thead>
<tr>
<th>Factor</th>
<th>Description of Variable</th>
<th>Factor Loadings</th>
<th>% Variance Explained</th>
<th>Eigen Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVO4</td>
<td>Effective approach to identify future environmental liabilities and the ability to tackle them without cost consideration</td>
<td>.922</td>
<td>60%</td>
<td>5.920</td>
</tr>
<tr>
<td>EVO5</td>
<td>Product and brand differentiation</td>
<td>.898</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVO2</td>
<td>Building firms reputation through sincere environmental stewardship</td>
<td>.883</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVO1</td>
<td>Innovation</td>
<td>.875</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVO6</td>
<td>Prior assessment of future environmental legislation</td>
<td>.868</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVO3</td>
<td>Proactive corporate policy</td>
<td>.834</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVO8</td>
<td>Cost saving and liability reduction</td>
<td>.932</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVO7</td>
<td>Customer concern for environment</td>
<td>.867</td>
<td>27%</td>
<td>1.058</td>
</tr>
</tbody>
</table>

After establishing the proposed measurement, the model hypotheses are tested using Structural Equation Modelling (SEM) technique \[68\] using the maximum likelihood method. The goodness of fit for a proposed model is checked by using SEM. The SEM is also used for testing the hypothesised paths between constructs. According to \[68\], the stability of measured items is confirmed by examining loading estimates. The parameters are considered stable when the loadings do not show any substantial change. This is also known as a measurement model validity. In the case of the present study, the chi-square statistics are estimated for checking ‘p’ value for overall model fit.

6. Results

The earlier section explains the results of reliability statistics, KMO and Bartlett’s test, total variance and factor analysis. The following part explains the results of CFA and SEM.

Figure 2 shows the hypothesised confirmatory factor analysis model.
Figure 2. Hypothesised confirmatory factor analysis

Figure 3 represents the standardised estimate output path diagram for the hypothesised confirmatory factor analysis model.

The results of the CFA analysis are shown in Table 6.

Table 6. Regression weights

<table>
<thead>
<tr>
<th></th>
<th>Estimate</th>
<th>S.E.</th>
<th>C.R.</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVO1 ← PES</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVO2 ← PES</td>
<td>.890</td>
<td>.037</td>
<td>24.149</td>
<td>***</td>
</tr>
<tr>
<td>EVO3 ← PES</td>
<td>.941</td>
<td>.034</td>
<td>27.710</td>
<td>***</td>
</tr>
<tr>
<td>EVO4 ← PES</td>
<td>1.005</td>
<td>.037</td>
<td>27.465</td>
<td>***</td>
</tr>
<tr>
<td>EVO5 ← PES</td>
<td>.899</td>
<td>.038</td>
<td>23.920</td>
<td>***</td>
</tr>
<tr>
<td>EVO6 ← PES</td>
<td>.858</td>
<td>.035</td>
<td>24.830</td>
<td>***</td>
</tr>
<tr>
<td>EVO7 ← PES</td>
<td>.548</td>
<td>.048</td>
<td>11.510</td>
<td>***</td>
</tr>
<tr>
<td>EVO8 ← PES</td>
<td>.404</td>
<td>.047</td>
<td>8.676</td>
<td>***</td>
</tr>
</tbody>
</table>

p value *** indicates that significance is smaller than 0.001 which signifies that the regression weights are different from zero and hence we conclude that that hypothesised relationship is significant. Similarly, significance of estimated covariance among the latent variables, as shown in Table 7 is assessed, if critical ratio C.R. > 1.96, the factor covariance is significant. The values of C.R. for the analysis are > 1.96 for all indicators; hence, the factor covariance is significant.

Table 7. Variances

<table>
<thead>
<tr>
<th></th>
<th>Estimate</th>
<th>S.E.</th>
<th>C.R.</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>3.527</td>
<td>.358</td>
<td>9.859</td>
<td>***</td>
</tr>
<tr>
<td>e1</td>
<td>.715</td>
<td>.080</td>
<td>8.976</td>
<td>***</td>
</tr>
<tr>
<td>e2</td>
<td>.689</td>
<td>.067</td>
<td>10.217</td>
<td>***</td>
</tr>
<tr>
<td>e3</td>
<td>.733</td>
<td>.074</td>
<td>9.963</td>
<td>***</td>
</tr>
<tr>
<td>e4</td>
<td>.496</td>
<td>.056</td>
<td>8.881</td>
<td>***</td>
</tr>
<tr>
<td>e5</td>
<td>.528</td>
<td>.057</td>
<td>9.235</td>
<td>***</td>
</tr>
<tr>
<td>e6</td>
<td>.575</td>
<td>.057</td>
<td>10.025</td>
<td>***</td>
</tr>
<tr>
<td>e7</td>
<td>1.931</td>
<td>.167</td>
<td>11.587</td>
<td>***</td>
</tr>
<tr>
<td>e8</td>
<td>2.038</td>
<td>.173</td>
<td>11.807</td>
<td>***</td>
</tr>
</tbody>
</table>

Cmin/df < 3 indicates an acceptable fit between the hypothesised model and sample data. According to the model fit summary, as shown in Table 8, the value of Cmin/df is 1.653, which is acceptable.

Table 8. Model fit summary

<table>
<thead>
<tr>
<th></th>
<th>CMIN (Chi Square Value)</th>
<th>NPAR</th>
<th>CMIN</th>
<th>DF</th>
<th>P</th>
<th>CMIN/DF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22</td>
<td>23.135</td>
<td>14</td>
<td>.058</td>
<td>1.653</td>
<td></td>
</tr>
</tbody>
</table>

Baseline Comparisons

<table>
<thead>
<tr>
<th></th>
<th>NFI</th>
<th>RFI</th>
<th>I FI</th>
<th>TLI</th>
<th>rho1</th>
<th>rho2</th>
<th>CFI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delta1</td>
<td>.991</td>
<td>.982</td>
<td>.996</td>
<td>.993</td>
<td>.996</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delta2</td>
<td>.996</td>
<td>.996</td>
<td>.996</td>
<td>.996</td>
<td>.996</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

RMR (Root Mean Square Residual)

<table>
<thead>
<tr>
<th></th>
<th>RMR</th>
<th>GFI</th>
<th>AGFI</th>
<th>PGFI</th>
</tr>
</thead>
<tbody>
<tr>
<td>GFI</td>
<td>.980</td>
<td>.949</td>
<td>.381</td>
<td></td>
</tr>
</tbody>
</table>

RMSEA (Root Mean Square Error of Approximation)

<table>
<thead>
<tr>
<th></th>
<th>RMSEA</th>
<th>LO 90</th>
<th>HI 90</th>
<th>PCLOSE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>.048</td>
<td>.000</td>
<td>.082</td>
<td>.489</td>
</tr>
</tbody>
</table>

Comparative Fit Index (CFI) evaluates the superiority of the tested model over the alternative model with manifest covariance matrix \(^6^9\). The CFI value for the current study is 0.996 and is acceptable. "Normed Fit Index" (NFI), the proportion in the improvement of the overall fit of the hypothesised model compared to the independent model, theoretically ranges from 0 (poor fit) to 1 (perfect fit), considered satisfactory when > .90. For the study, NFI is 0.991 and is highly acceptable.

Similarly, Goodness of Fit Index (GFI) theoretically ranges from 0 to 1, considered satisfactory when > .90. The GFI obtained for the study is 0.980, which is ideal. "Adjusted Goodness of Fit Index" (AGFI), like GFI but adjusts for model complexity (like adjusted multiple r-squared), is considered satisfactory when > .90. AGFI for the study is 0.949 and is therefore acceptable. "Root Mean Square Error of Approximation" (RMSEA), calculates the size of the standardised residual correlations, considered acceptable when < .05. Value of RMSEA obtained is 0.048. From the model fit summary represented in Table 8, it is concluded that the hypothesised model is supported statistically. The results of the hypotheses are

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were proactive towards environmental protection. Based on the questionnaire, 280 valid responses were received. SEM supported all the proposed eight hypotheses.

According to hypothesis H1, innovation is considered to be positively associated with PES adoption. The analyses support the hypothesis. According to [77], technological innovations are considered as key requirements for sustainable development. Hypothesis H2 proposed environmental stewardship as a positive indicator of PES adoption. As reported in several studies [45, 70], environmental stewardship involves trade-offs between efficiency and resilience along with near and long-term benefits. Thus environmental stewardship benefitted the firms adopting PES. A defined environmental policy is always better to deal with any adverse condition arising due to environmental damage. The firms having a defined environmental policy were able to get relief from the regulatory authorities which benefitted the firms investing in environmental systems [47].

Thus, the analyses rightly support the hypothesis H3 which proposes defined environmental policy as a positive indicator of environmental proactivity. To protect their business interests, the firms in the emission intensive area must adopt an effective approach to identify future environmental liabilities as any change in regulation may severely affect its business. [49] studied the initiatives taken by the firms’ in the early 1990s to anticipate the adverse environmental impact of their operations and measures taken for reducing pollution and waste before regulation. This resulted in an optimistic approach to taking benefit of business opportunities by adopting total quality environmental management. The analyses rightly support hypothesis H4 which proposes an effective approach to identify future environmental liabilities as a positive indicator of firms’ environmental proactiveness. For any firm to have a positive image in the market, it creates a product and brand differentiation. With increased consumer awareness and stringent environmental regulations, the green brand image of the firm helps in a smooth business transaction

7. Conclusion

7.1 Discussion of Results

The Indian power sector has witnessed a dynamic change since the 1950s from the coal-based highly polluting power plants to the ultra-modern super thermal power plants. Due to the absence of basic infrastructure in the early 1950s, the primary focus was to establish the power plants with the technology which was available during that period. With the rapid growth in industrialisation, demand for power increased manifold, which resulted in consumption of widely available coal and greater emissions. With the increase in awareness towards increasing adverse effects of emissions on the ecology, the environmentalists pressurised the governments to evolve policies for controlling the environmental damage. The Indian power sector, which was a state monopoly witnessed the entry of private firms which were equipped with better technologies and were more transparent in environmental reporting. However, inspite of regulatory norms for environmental protection, several firms were observed to be more conscious of environmental damage. Normally for a business entity bare minimum compliance of regulatory norms is observed. So, what prompted these firms to go beyond the extant laws to adopt proactive environmental strategies? The study was conducted to identify the factors based on the literature review and annual reports of the firms who were proactive towards environmental protection. Based on the study, several factors were observed to be positively associated with the adoption of PES. These factors are mentioned in Table 9.

<table>
<thead>
<tr>
<th>No.</th>
<th>Hypothesis</th>
<th>Significance</th>
<th>Accepted</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>Innovation is positively associated with the adoption of PES</td>
<td>***</td>
<td>Yes</td>
</tr>
<tr>
<td>H2</td>
<td>Sincere environmental stewardship is positively associated with the adoption of PES</td>
<td>***</td>
<td>Yes</td>
</tr>
<tr>
<td>H3</td>
<td>Defined environmental policy is positively associated with the adoption of PES</td>
<td>***</td>
<td>Yes</td>
</tr>
<tr>
<td>H4</td>
<td>Effective approach to identify environmental liabilities and the ability to tackle them without cost consideration is positively associated with the adoption of PES</td>
<td>***</td>
<td>Yes</td>
</tr>
<tr>
<td>H5</td>
<td>Product and brand differentiation is positively associated with the adoption of PES</td>
<td>***</td>
<td>Yes</td>
</tr>
<tr>
<td>H6</td>
<td>Prior assessment of future environmental legislation is positively associated with the adoption of PES</td>
<td>***</td>
<td>Yes</td>
</tr>
<tr>
<td>H7</td>
<td>Customer concern for the environment is positively associated with the adoption of PES</td>
<td>***</td>
<td>Yes</td>
</tr>
<tr>
<td>H8</td>
<td>Cost saving and liability reduction is positively associated with the adoption of PES</td>
<td>***</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Note: *** highly significant at p < 0.001
hypothesis H₇, proposing customer concern for the environment to have a positive association with PES adoption, it is recommended by the economists that firms can influence their customers by taking voluntary action for environmental protection and creating a market for products having low carbon footprints. The study finds the association positive in H₇. Finally, according to hypothesis H₈, cost saving and liability reduction are positively associated with the adoption of PES. The analyses find a positive association and support the hypothesis. According to these studies support the analyses outcome, which supports the hypothesis H₈.

7.2 Limitations and Scope for the Future Study

Even though the results reflect that the environment vanguard firms in the Indian power sector are more environmentally proactive than their counterparts, there are limitations to the study. The industry specific and country specific limitations point to investigate whether other industries and countries have the same outcome. Not all industries may have the same level of vertical integration across the environmental policies, nor might there be visible environment implications from their operations. Thus, these industry differences need to be investigated. Another limitation of the study is whether the small companies in the power sector show similar behaviour as compared to their multinational counterparts. Such a study can throw light on the outcome of the adoption of PES by small and big companies in the power sector.

Although the findings of the empirical study are meaningful, the empirical research on sector specific study in India is limited. This empirical research focuses only on explaining the adoption of PES by the power sector in India. The other key sectors, which are also contributors to infrastructure development, need to be investigated. Very limited work is available on sector specific studies, and more studies are required. Further, a specific study on noncompliance with environmental regulations will also throw light on the issue. Another important study can examine the effect of regulatory capacity and its ability to enforce regulations along with institutional regulatory structure with its implications on environmental strategies of the firms.

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**REVIEW**

**A workflow to Predict the Present-day in-situ Stress Field in Tectonically Stable Regions**

**Wei Ju**¹ ²,  
**Ke Xu**³,  
**Jian Shen**¹ ²,  
**Chao Li**²,  
**Guozhang Li**²,  
**Haoran Xu**²,  
**Shengyu Wang**²

¹. Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process, Ministry of Education, China University of Mining and Technology, Xuzhou, Jiangsu, 221008, China
². School of Resources and Geosciences, China University of Mining and Technology, Xuzhou, Jiangsu, 221116, China
³. PetroChina Tarim Oilfield Company, Korla, Xinjiang, 841000, China

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**ABSTRACT**

Knowledge of the present-day in-situ stress distribution is greatly important for better understanding of conventional and unconventional hydrocarbon reservoirs in many aspects, e.g., reservoir management, wellbore stability assessment, etc. In tectonically stable regions, the present-day in-situ stress field in terms of stress distribution is largely controlled by lithological changes, which can be predicted through a numerical simulation method incorporating specific mechanical properties of the subsurface reservoir. In this study, a workflow was presented to predict the present-day in-situ stress field based on the finite element method (FEM). Sequentially, it consists of: i) building a three-dimensional (3D) geometric framework, ii) creating a 3D petrophysical parameter field, iii) integrating the geometric framework with petrophysical parameters, iv) setting up a 3D heterogeneous geomechanical model, and finally, v) calculating the present-day in-situ stress distribution and calibrating the prediction with measured stress data, e.g., results from the extended leak-off tests (XLOTs). The approach was successfully applied to the Block W in Ordos Basin of central China. The results indicated that the workflow and models presented in this study could be used as an effective tool to provide insights into stress perturbations in subsurface reservoirs and geological references for subsequent analysis.

**1. Introduction**

In-situ stress refers to the internal stress within the Earth’s crust, which is closely related to gravitational and tectonic stresses¹⁹. Knowledge of the present-day in-situ stress distribution is greatly important in a wide range of fields including oil and gas exploration and development²,⁷,¹⁵,¹⁶,¹⁷,¹⁹,²³, wellbore stability assessment¹³,²³,²⁵, reservoir management¹²,¹⁵, and CO₂ sequestration¹⁵, etc.

In general, plenty of factors, e.g., the development of faults, contrasts in rock mechanical properties, and basement structures, etc. can cause stress perturbations and produce local stresses that may significantly deviate from the regional stress field¹⁸,¹⁹. Therefore, within a reservoir scale, stress...
magnitudes and orientations are frequently not homogeneous, which may lead to incorrect pre-drilling prediction[9].

In tectonically stable regions, faults and folds are usually not developed, and the present-day in-situ stress variations may be largely controlled by lithological changes. Currently, the majority of available two-dimensional (2D) and simple three-dimensional (3D) models are not suitable for understanding stress distributions because the whole reservoir or layer is regarded as homogeneous and assigned identical mechanical parameters. Such assumptions are often inconsistent with the actual geological conditions, resulting in relatively large errors during stress field simulations[18,20]. Therefore, complex 3D heterogeneous models with specific mechanical properties of the subsurface reservoir are required to obtain quantitative understandings of the present-day in-situ stress distributions.

In this study, a workflow consisting of 3D heterogeneous models has been developed to predict the present-day in-situ stress distribution with a case study in the Block W of Ordos Basin. The FEM has been proven to be a valid approach to address such reservoir issues[11,12]. The results in this study were verified with measured stress data, suggesting the proposed workflow could be used as an effective tool for predicting the present-day in-situ stresses and hence providing some important geological references in subsequent analysis of a given reservoir.

2. The General Workflow for Stress Field Prediction in Tectonically Stable Regions

The finite element (FE) technique was utilized in this study to gain quantitative insights into the present-day stress distributions because this approach allows complex geometries and heterogeneous mechanical properties. In this study, a workflow was developed to predict the present-day in-situ stress field with five steps shown in Figure 1. The details were described in the following sections.

2.1 3D Geometric Framework

The first step of this workflow development is to build a 3D geometric framework, which is generally labor-intensive. The FE software ANSYS (Ansys Inc., Houston, USA) was employed to construct the 3D geometric framework of a given reservoir in this study. A typical framework building procedure generally includes a few sub-steps as outlined as follows:

(1) Choosing an appropriate element type. For solving this kind of issue, the elements of Solid 185 and Solid 186 within the ANSYS software are the proper choices.

(2) Generating different solid model features from the bottom up. That is, create key points, and then define lines, arcs, and volumes as needed. Commonly, the initial input data for different layer surfaces are derived from interpretation of available 3D seismic.

(3) Applying the Boolean operators or specific number controls to join separate solid model regions together as appropriate.

(4) Setting meshing controls to establish desired mesh density, and creating nodes and elements by meshing the solid model. The spatial resolutions and element sizes inside the model are controlled by the study area scale and device conditions.

2.2 Petrophysical Parameters

Creating a 3D petrophysical parameter field is completed in the Petrel E&P software platform (Schlumberger Limited, Houston, USA), which is also labor-intensive. The general outline follows:

(1) Data (well heads, well tops and well logs, etc.) preparation and loading. Well heads contain the position of each well and measured depth along the path. Well tops are the markers representing significant points. Well logs include basic logs (density, gamma curve, acoustic log, etc.) and calculated logs (Young’s modulus, Poisson’s ratio, etc.).

(2) Structural modeling, which includes pillar gridding, makeup horizons, and layering. Pillar gridding is the process of generating the grid, the size of which should be at the same level as the element size in the ANSYS software. Makeup horizons and layering are used for vertical divisions.

(3) Property modeling, including scale up well logs and petrophysical modeling. Scale up well logs will average the values to the cells in the 3D grid. Petrophysical modeling is the process of assigning petrophysical property values to each cell of the 3D grid using geostatistical methods, e.g., the Sequential Gaussian Simulation Algorithm.

2.3 Integrating 3D Geometric Framework with Petrophysical Parameters

The grids used for property modeling and flow simulations in the Petrel E&P software platform are different from those in the FE ANSYS software. Hence, it is necessary to integrate the previously built geometric framework with petrophysical parameters so as to build a 3D heterogeneous geological model. The procedure of integrating 3D geometric framework with petrophysical parameters is given as follows:

(1) Exporting petrophysical parameters, including rock density, Young’s modulus, and Poisson’s ratio, from Petrel E&P software platform combined with corresponding cell center xyz coordinates.

(2) Calibrating these mechanical properties utilizing static ones obtained from rock mechanics experiments on drill
(3) Setting a “searching length” for the connections between cells in the Petrel E&P software platform and elements in ANSYS software, which is determined based on the element size.

(4) Integrating the framework with petrophysical parameters by means of the ANSYS Parametric Design Language (APDL), and thus, the 3D heterogeneous geological model is built. The codes for this implementation are listed in the Appendix.

2.4 3D Heterogeneous Geomechanical Model

Applying suitable boundary forces and displacements to the 3D heterogeneous geological model obtained from Section 2.3 will construct the geomechanical model, as described in the following procedure:

(1) Determining the applied boundary force orientations. Those can be derived from interpretations of borehole stress-induced failures (e.g., borehole breakout and drilling-induced tensile fracture [14,15,25], paleomagnetic analysis [24], earthquake focal mechanism inversion [10,22], etc.

(2) Determining the applied boundary force magnitudes. Vertical force magnitudes are generally calculated from the bulk density of rocks and can be automatically applied in the ANSYS software by setting the gravitational acceleration. Initial horizontal force magnitudes are commonly obtained from the regional analysis.

(3) Determining the applied boundary displacements. Commonly, the top portion is set as a free surface and the bottom is fixed with respect to vertical movements.

2.5 Prediction of In-situ Stress Distribution and Validation

Finally, the geomechanical model is numerically solved to obtain the present-day in-situ stress distributions. The results are further calibrated with measured stress data for validation, e.g., the extended leak-off tests (XLOTs).

(1) The geomechanical model developed above is numerically solved through the linear static structural analysis solver in the FE ANSYS software.

(2) The calibration and validation are carried out by comparing the calculated stresses with actually measured stress data, e.g., the extended leak-off tests (XLOTs) [15,25] and the acoustic emission experiment on drill cores [6]. If most of the calculated errors are relatively low, ranging between -0.1 and 0.1, the calculated stresses will be used for predicting the present-day in-situ stress distribution. Otherwise, the geomechanical model requires rebuilt by repeating previous procedures.

3. A case Study in the Block W of Ordos Basin

The workflow outline presented above is applied to the Block W of Ordos Basin, central China, within which, faults and folds are not developed. It is a tectonically stable region with flat sedimentary layers. The Block W is an important area for unconventional gas production in the Ordos Basin of China, including tight sandstone gas and coalbed methane (CBM). For example, the L Formation acts as one of the most economic tight sandstone gas reservoirs within the Block W.

First, the 3D geometric framework (Figure 2) and 3D petrophysical parameter field (Figure 3) for the Block W were built utilizing the ANSYS software and Petrel E&P software platform, respectively. The 3D geometric framework was integrated with petrophysical parameters by using those codes in the Appendix.

Figure 2. The 3D geometric framework for the Block W in Ordos Basin, central China

Interpretations of borehole breakouts and DITFs indicated that the horizontal maximum principal stress ($S_{Hmax}$) orientation was ~E-W-trending within the Block W (Figure 4). Multiple attempts have been made in simulation in terms of the calibration utilizing the XLOTs results from...
four wells (Table 1) within the study area to obtain the best fit present-day stress distributions (Figure 5).

**Figure 3.** The 3D distributions of dynamic Young’s modulus (a) and dynamic Poisson’s ratio (b) for the Block W in Ordos Basin

*Note:* $E$ is the dynamic Young’s modulus (GPa), $\mu$ is the dynamic Poisson’s ratio, and vertical exaggeration $\times 5.0$.

**Table 1.** The comparison between actually measured and modelled stress magnitudes in the Block W of Ordos Basin

<table>
<thead>
<tr>
<th>Well</th>
<th>Measured minimum principal stress magnitude (MPa)</th>
<th>Modelled minimum principal stress magnitude (MPa)</th>
<th>Error$^{(a)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-3</td>
<td>26.89</td>
<td>29.23</td>
<td>0.0870</td>
</tr>
<tr>
<td>W-6</td>
<td>37.63</td>
<td>28.99</td>
<td>-0.2296</td>
</tr>
<tr>
<td>W-7</td>
<td>29.87</td>
<td>30.88</td>
<td>0.0338</td>
</tr>
<tr>
<td>W-8</td>
<td>28.42</td>
<td>31.01</td>
<td>0.0911</td>
</tr>
</tbody>
</table>

*Note:* $(a)$ the error is calculated based on the equation of (modelled data - measured data)/measured data.

The plots shown in Figure 5 nicely display and elucidate the present-day in-situ stress perturbations in the L Formation, which can be used for numerous applications within the Block W of Ordos Basin, e.g., guiding the development of tight sandstone gas.

**4. Conclusions**

A better understanding of a reservoir largely relies on the sufficient knowledge of present-day in-situ stresses, which contributes to successful gas exploration and production, hydraulic fracturing design and borehole stability. In tectonically stable regions, conventional 2D and simple 3D models can not reveal the specific present-day in-situ stress perturbations. The complex 3D heterogeneous models were developed to provide the fundamental base for a general workflow to predict the present-day in-situ stress field. The workflow consists of five steps, namely, (1) building a three-dimensional (3D) geometric framework, (2) creating a 3D petrophysical parameter field, (3) integrating the geometric framework with petrophysical parameters, (4) setting up a 3D heterogeneous geomechanical model, and finally, (5) calculating the present-day in-situ stress distribution and calibrating the prediction with measured stress data. The workflow was further presented in details by implementing it to the Block W of Ordos Basin as a case study. The results indicated that this proposed workflow can be used to accurately predict the present-day stress field in tectonically stable regions. The information on the in-situ stress distribution can be used for improved plannings of numerous applications.
It is assumed that positive values are compressive stresses in this study.

Acknowledgments

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Appendix

The ANSYS Parametric Design Language (APDL) codes for integrating the geometric framework with petrophysical parameters are listed as follows:

```plaintext
/prep7
aa=lines of property data
*dim,mpara1,aa,6,,
*vread,mpara1(1,1),property data text name,txt,,jik-,6,aa,,0,
(6F13.3)
*do,i,1,aa
mp,ex,i,mpara1(i,4)
mp,prxy,i,mpara1(i,5)
mp,dens,i,mpara1(i,6)
*endo
ox=initial x value
yo=initial y value
zo=initial z value
*do,i,1,aa
mpara1(i,1)=mpara1(i,1)-xo
mpara1(i,2)=mpara1(i,2)-yo
mpara1(i,3)=mpara1(i,3)-zo
*endo
*do,e1,1,element number
xx=0
yy=0
zz=0
*do,ni,1,4
xx=xx+nx(nelem(ei,ni))
yy=yy+ny(nelem(ei,ni))
zz=zz+nz(nelem(ei,ni))
*endo
xx=xx/4
yy=yy/4
zz=zz/4
ldist=searching length
rowi=1
*do,di,1,aa
dist1=(mpara1(di,1)-xx)**2+(mpara1(di,2)-yy)**2+(mpara1(di,3)-zz)**2
*if,dist1,le,ldist,then
ldist=dist1
rowi=di
*endif
*endo
eomodif,ei,mat,rowi
*endo
```

References

[10] Heidbach, O., Rajabi, M., Cui, X.F., Fuchs, K., Müller, B., Reinecker, J., Reiter, K., Tingay, M.,


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  The corresponding author should be identified.
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● A brief description of the novelty and importance of the findings detailed in the paper

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Sub-Headings: Font size 16, bold type
Sub-Subheadings: Font size 14, bold type

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Equations should be aligned to the left, and numbered with in running order with its number in parenthesis (aligned right).

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