Mossbauer spectroscopic study of soils collected from Panipat region

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Mossbauer spectroscopy of $^{57}$Fe has been used to study some soil samples picked up from regions where the growth of crops is not normal as well as from the fertile part of the land in the Panipat district of Haryana. The ferrous-ferric ratios in these samples were determined. An attempt has also been made to correlate the Fe$^{3+}$/Fe$^{2+}$ ratio with pH values of the samples. The importance of these results lies in the necessity of application of suitable micronutrients in the area where the growth of crops is below normal.

1 Introduction

Iron contents in soil samples of Panipat region in India has been undertaken in this study, as it is one of the main inorganic constituents of the plant leaves. It monitors respiration and photosynthesis in the plants. Iron is essential for synthesis of proteins in chloroplasts and it also regulates the uptake of other micronutrients from soil. Iron is mostly absorbed by the plants in Fe$^{3+}$ form. Thus, ferrous/ferric ratio may be used as an index of availability of iron, which can be taken up by the plants.

The Mossbauer technique enables us to distinguish between the two important oxidation states of iron (Fe$^{3+}$ and Fe$^{2+}$) that occur in different soils under natural conditions. Accurate estimates of Fe$^{3+}$/Fe$^{2+}$ ratio are very crucial in the field of agriculture, as this ratio can be taken as a measure of the degree of iron deficiency and hence an index of suitability of micronutrients.

2 Experimental Procedure

The samples were powdered and sieved through a 200 µm gauge. The absorbers were so prepared that areal density was 50 mg/cm$^2$ with a uniform spread. The absorption spectra were recorded in transmission geometry, at room temperature, with a constant acceleration Mossbauer drive and a 256 multi-channel analyzer, using a Austin Science Inc., USA Mossbauer spectrometer. A single line 10 mCi, $^{57}$Co source in the Rh matrix was used. In general, several runs were taken to check the reproducibility of the spectra. Total counts collected per channel were close to 10$^5$ or more.

The Mossbauer spectrometer was calibrated using a 1ML, enriched α-Fe foil. The outer-most lines were separated through 10.56 mm/s. This is in excellent agreement with an ideal absorption spectrum and calibration was done accordingly. One channel corresponds to a velocity of 0.0625 mm/s. The experimental data were fitted using a least-squares fitting program, assuming Lorentzian line-shape.

3 Results and Discussion

Mossbauer spectra of all the samples were recorded at room temperature, in transmission geometry. The spectra were computer-fitted and the hyperfine parameters, i.e. isomer shift ($\delta$) mm/s, quadrupole splitting ($\Delta$) mm/s and line-width (Γ) mm/s are listed in Table I. On the basis of computed values of isomer shift and quadrupole splitting the Fe$^{3+}$ and Fe$^{2+}$ states were assigned to doublet components in the spectra, using the procedure of other workers. All the spectra were analysed by the least-square fitting computer programme for one and two doublets having Lorentzian shapes using $\chi^2$ minimization technique. The absorption spectra were analysed to identify Fe$^{3+}$ and Fe$^{2+}$ states of iron that occur in the soil samples under study. In the spectrum of sample SL-1 (Fig. 1) the doublet AA$^*$ is assigned to Fe$^{3+}$ and the doublet BB$^*$ assigned to Fe$^{2+}$. The Mossbauer...
spectra of the sample BL-1 is shown in Fig. 2, and is double that corresponding to Fe$^{3+}$ state.

The Fe$^{2+}$/Fe$^{3+}$ ratio has been determined from the area method in the following manner. If a thin absorber sample contains iron atoms in two different chemical states that give well-resolved Mossbauer spectra of area $A_1$ and $A_2$, then $A_1/A_2 = n_1/n_2$, where $n_1$ and $n_2$ are the total number of iron atoms of the ferrous and ferric type, respectively. This is true when the full width at half maxima of the Mossbauer line corresponding to two types of iron and their recoil-free fractions are equal in a very thin sample at a given temperature. The results obtained in the present work are listed in Table 1. These results have been analysed keeping in view the work of other authors.

Table 1 — Hyperfine parameters for soil samples from Panipat, India, computed from Mossbauer spectra recorded at room temperature. Isomer shift $\delta$ is given relative to $\alpha$-Fe.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Site</th>
<th>Isomer shift $\delta$ (mm/s)</th>
<th>Quadrupole splitting $\Delta$ (mm/s)</th>
<th>Line-width $\Gamma$ (mm/s)</th>
<th>$\chi^2$/degree of freedom</th>
<th>Forms of iron</th>
<th>Colour</th>
<th>Fe$^{2+}$/Fe$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SL-1</td>
<td>AA'</td>
<td>0.67</td>
<td>2.60</td>
<td>0.72</td>
<td>0.55</td>
<td>Fe$^{2+}$</td>
<td>Grey</td>
<td>0.974</td>
</tr>
<tr>
<td></td>
<td>BB'</td>
<td>0.28</td>
<td>0.68</td>
<td>0.33</td>
<td></td>
<td>Fe$^{2+}$</td>
<td></td>
<td></td>
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<tr>
<td>SL-2</td>
<td>AA'</td>
<td>0.69</td>
<td>2.64</td>
<td>0.56</td>
<td>0.74</td>
<td>Fe$^{2+}$</td>
<td>Grey</td>
<td>0.672</td>
</tr>
<tr>
<td></td>
<td>BB'</td>
<td>0.32</td>
<td>0.73</td>
<td>0.34</td>
<td></td>
<td>Fe$^{2+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BL-1</td>
<td>BB'</td>
<td>0.21</td>
<td>0.87</td>
<td>0.30</td>
<td>0.55</td>
<td>Fe$^{2+}$</td>
<td>White-grey</td>
<td>---</td>
</tr>
<tr>
<td>BL-2</td>
<td>BB'</td>
<td>0.34</td>
<td>0.68</td>
<td>0.32</td>
<td>1.23</td>
<td>Fe$^{2+}$</td>
<td>White-grey</td>
<td>---</td>
</tr>
<tr>
<td>BL-3</td>
<td>BB'</td>
<td>0.30</td>
<td>0.61</td>
<td>0.31</td>
<td>1.02</td>
<td>Fe$^{2+}$</td>
<td>White-grey</td>
<td>---</td>
</tr>
</tbody>
</table>

The Fe$^{2+}$/Fe$^{3+}$ ratio for the samples of the present study is consistent with the work reported by Eslinger et al., given in Table 1 and are also in agreement with the results reported by Das et al.. Iron in the ferrous state is preferentially absorbed for plant nutrition. Therefore, the present work establishes that, the soils from the region where the crops growth is not satisfactory, mostly contain Fe$^{2+}$ state and hence suffer from deficiency in respect of plant nutrition. The results are also useful as an index of availability of ferrous iron as micronutrients for plant growth and productivity. The Fe$^{2+}$/Fe$^{3+}$ ratio is important, because many of the soil samples analysed and shown in Table 1 contain iron in Fe$^{2+}$ state, which, in soil, does not
serve as micronutrient for plants. Results of the authors are also consistent with those reported by Eslinger et al.\textsuperscript{5}. The pH value of the soil samples dissolved in distilled water and filtered, was observed by using pH indicator supplied by Glaxo India Ltd. The observed pH value of the soil samples SL-1 and SL-2 varies from 7.0 to 7.5, while the soil sample BL-1, BL-2 and BL-3 varies from 9.5 to 10. In the soil samples having pH values from 7.0 to 7.5, both Fe\textsuperscript{3+} and Fe\textsuperscript{2+} states exist, while in those in the pH range 9.5-10.0, only Fe\textsuperscript{2+} state is found to be present. This shows that, Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio decreases with increase of pH. Thus, the findings can be useful for determining the degree of artificial micronutrients requirement for the soil, where the iron is in the form of Fe\textsuperscript{3+} state.

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References