

# Determination of plant nitrogen requirement using Surface-Enhanced Raman Spectroscopy and optimum use of fertilizers

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**Abstract:** Raman and near-infrared spectroscopies were used to estimate the plant nitrogen uptake and loss due to emission in fertilized canola plots, which will assist in monitoring the crop's nitrogen requirement and minimize the fertilizer usage.

Nitrogen (N) is an essential nutrient for plant growth and survival. It is an important component of chlorophyll and amino acids. Plants get N from the soil through their roots. However, a small percentage of the available N in the soil is suitable for uptake and is not sufficient to satisfy the crop's needs. So, farmers supplement soil N by applying N-fertilizers. Fig. 1 (a) shows the pathways of N-loss and N-uptake by plants after application of N fertilizers. A substantial amount of N is lost by: (1) volatilization, which emits Ammonia (NH<sub>3</sub>) gas in the atmosphere; (2) leaching – translocation of dissolved N outside of the crop-soil system. Excessive N fertilizer could result in an increased N-loaded runoff into rivers and lakes during and after rain or irrigation, polluting those water bodies, and (3) denitrification, which emits Nitrous Oxide (N<sub>2</sub>O), Nitrogen Oxide (NO<sub>2</sub>), Nitric Oxide (NO) and Diatomic Nitrogen (N<sub>2</sub>). To enhance fertilizer use efficiency, economic returns, and sustainability, accurate assessment of N – requirement and real-time spatial data on N content in plants during different growth stages of crops is essential.

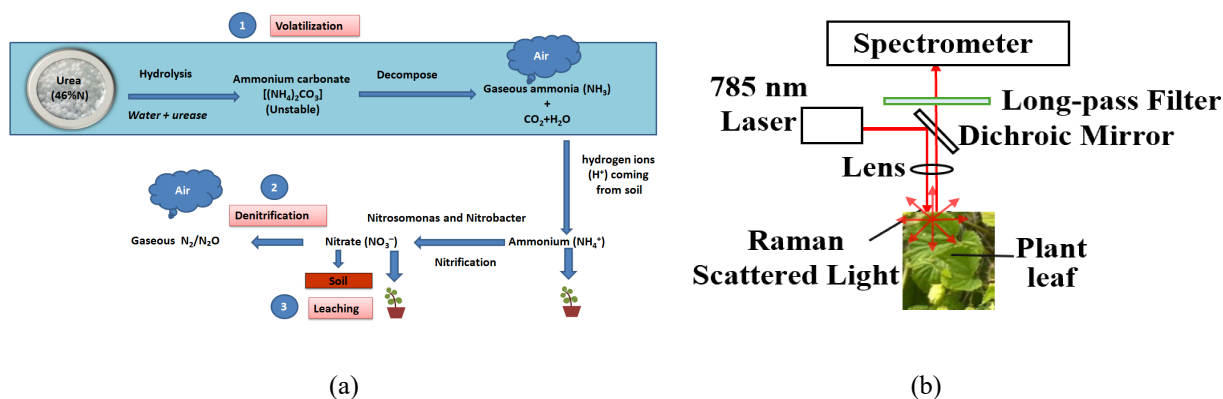


Fig 1. (a) Nitrogen pathways after application of Urea fertilizer, and (b) Raman Spectroscopy system

Raman Spectroscopy (iHR 550, Horiba, Fig. 1 (b)) and near-infrared (NIR) absorption spectroscopy (Picarro 2508) have established themselves as unique tools for detecting and quantifying trace amounts of chemicals [1,2]. We proposed and demonstrated a noninvasive method that integrates Raman spectroscopy and NIR absorption spectroscopy to estimate optimal use of fertilizers, which will bring economic benefits to farmers and reduce emissions from the fertilized agricultural fields and the environmental impact of the N fertilizers.

Further, Surface - enhanced Raman Spectroscopy (SERS) - has been widely used to enhance the weak Raman signal, which requires the manufacturing of the substrate based on metallic nanomaterials (e.g., gold nanorods) where analytes get adsorbed. A drop (~ few microliters) of gold nanorods (GNRs) solution was added on the surface of the canola leaves and obtained the Raman spectra, and the method does not need any substrate preparation.

The research was performed at the Lakehead University Agricultural Research Station (LUARS). Fig. 2 (a) shows Raman spectra obtained from canola leaves collected from plots (area 7.5 m<sup>2</sup>) treated with (i) 306.8 g of polymer-coated urea, (ii) 293.5 g of urea, and (iii) without fertilizer, at the flowering stage of the plants. The N rate from the two fertilizers was 180 kg N ha<sup>-1</sup>. To estimate the health of the plant or N-uptake, we compared the Raman peaks at ~ 910 cm<sup>-1</sup> and ~ 1046 cm<sup>-1</sup>, respectively [3, 4]. The presence of the GNRs (LSPR 1064 nm) enhanced the signal. One can obtain much higher enhancements by using GNRs with LSPR at 785 nm, which matches the excitation wavelength of laser [1].

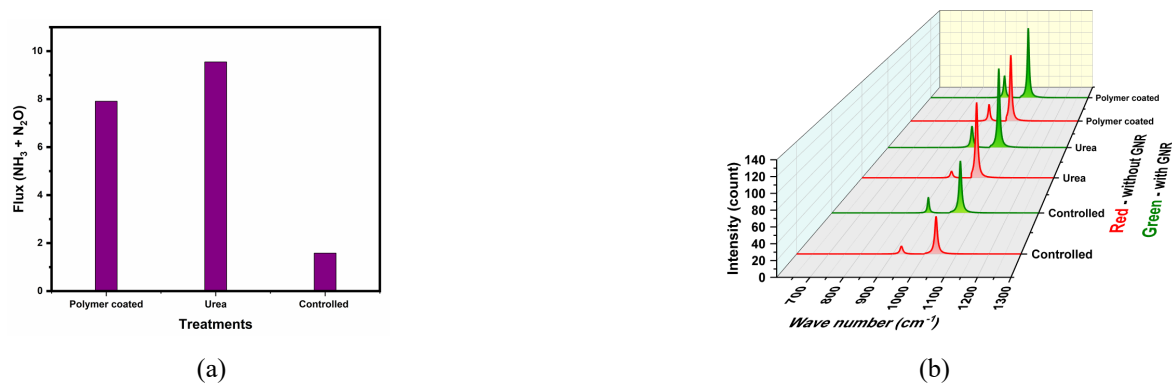


Fig. 2. (a) Raman Peaks at ~ 910 cm<sup>-1</sup> and ~ 1046 cm<sup>-1</sup>, and (b) N loss due to gas emission (NH<sub>3</sub> and N<sub>2</sub>O).

Fig. 2(a) presents average nitrogen losses via N<sub>2</sub>O and NH<sub>3</sub> flux, measured 18 times between June and August 2025. While not continuous, these measurements provide a representative estimate of gaseous N loss. The control plot (no fertilizer) exhibited the lowest emissions, attributed to residual soil nitrogen (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>). In contrast, the urea-treated plot showed the highest flux, indicating substantial nitrogen loss and reduced availability for plant uptake. Notably, the polymer-coated urea plot had intermediate emissions, which were lower than urea, suggesting improved nitrogen retention in the soil.

The polymer-coated urea plot exhibited the strongest Raman signals, observed in Fig. 2 (b), indicating enhanced nitrogen uptake by the crop. These results, combined with the nitrogen flux measurements, suggest that polymer-coated fertilizers release nitrogen gradually, aligning better with plant demand. By measuring a reference N level using Raman Spectroscopy for a particular plant species in a geographical region, the development of real-time nitrogen monitoring systems using Raman spectroscopy—potentially replacing hyperspectral imaging - could be undertaken. Such precision fertilization strategies can adapt the application of fertilizer at the right time, based on the plant's requirements, not only reducing losses from emissions (N<sub>2</sub>O, which is a potent greenhouse gas), but also increasing economic benefits to farmers, as they would need to apply less fertilizer. The use of GNRs to obtain enhanced Raman signals is one of the significant contributions. We will present more results during our presentation.

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