## SPECIAL FEATURE: SOIL

Soil alchemy the dark mystery of dirt

While many aspects of the technology we use to examine soil have advanced, much of our knowledge still comes from discoveries made in the 19th century.

Leonardo Da Vinci said: "We know more about the movement of celestial bodies than about the soil underfoot". Many centuries and much research later, we continue to research the chemical interactions in the soils that grow our food. Soil is a complex matrix, and its chemical composition often depends on the location in the landscape, the parent material underneath and the influence of the management above. Defining chemical reactions in soil is akin to the art of alchemy. In fact, the word alchemy has its roots in the Arabic word *kimia* or *khem*, which refers to the fertile black soil of the Nile Delta.

In a series of lectures between 1800 and 1812, one entitled 'Elements of Agricultural Chemistry' described soil chemistry as "changes in the arrangements of matter connected with growth and nourishment of plants" and identified 47 elements from the periodic table as influential in these processes. Since then, we've become very adept at characterising and measuring these processes with advances in instrumentation and data science.

## Inside the soil matrix

Our soils are composed of sand, silt, clay, organic matter, water and air, and this matrix provides the infrastructure that allows chemical reactions to generate available nutrition for plant growth. The elements that constitute major and micro nutrients are dynamic and changeable, and can exist in different forms of availability and stability.

These transformations can happen in clay surfaces and organic matter, often called the engine room inside the soil matrix, and where many of the soil chemical and biological reactions occur. A healthy amount of soil organic matter (SOM) is essential for many of the processes that control nutrient supply and storage in soils, and if SOM is depleted or reduced, this inhibits the soil's ability to provide soluble forms of nutrients, and more importantly, its ability to store and sequester carbon. As we move towards low-emission agriculture, it is hugely important to protect and enhance our soil carbon stocks.

For essential nutrients such as nitrogen and phosphorus, these can be stored inside the soil matrix and made available when crops need them. A healthy soil will have the ability to immobilise (store) and mineralise (supply) nutrients, and this function relies on a number of soil properties to be in good working order. For nutrient supply to function at full capacity, other soil chemical conditions must be met, for example, soil pH provides the right environment for nutrients to become soluble and for reactions on clay surfaces to happen. As many chemical reactions happen in solution, soil moisture content becomes an important characteristic for nutrient diffusion to plant roots, and this links directly to soil structure, where soil drainage class, and amount and type of clays and organic matter play an important role.

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FIGURE 1 (from left): passive samplers deployment rig (A) and lab-on-a-disk (B) for in-situ nutrient analysis, both developed at the DCU Water Institute. (C) Bruker FTIR spectrometer used at Teagasc Johnstown Castle to scan soils.

## Chemical analysis: what's changed?

In the early years of soil science, the major themes in soil chemistry were dominated by ion exchange, clay mineralogy, soil acidity, sorption processes and kinetics, all in an effort to understand how to optimise soil fertility and plant nutrition. These themes are still relevant today in productive agricultural systems, but our focus has shifted towards the role of soils in protecting water quality, biodiversity and in mitigating climate change.

The emphasis has shifted to combining disciplines in soil physics and chemistry to understand the fate and transport of nutrients, pesticides and contaminants in soils to surface and groundwater at wider landscape scales. Combining soil biology and chemistry is helping us to understand the role of SOM in soil microbiota and for sequestering carbon, which is essential if we are to protect soil health and enhance our soil carbon stocks. Measuring and monitoring these parameters has also evolved over the years, although we still use some of the methods that have stood the test of time.

For example, traditional soil tests for nutrient availability date back to methods developed in the 1950s and remain the standardised methods in use today. Properties such as texture, particle size, ion exchange, pH, and acidity lend themselves to new, predictive methods such as soil spectroscopy and chemometrics. Near-infrared (NIR) and mid-infrared (MIR) light shone on a soil sample can produce an image or spectra, unique to each soil sample, as a fingerprint is unique to each individual. This fingerprint contains peaks, or information that we convert into data points, which we can use to quantify carbon, SOM, pH, particle size fractions, clay minerals, and cation exchange capacity, to name a few.

Advances in laser and optical techniques, coupled with machine learning in statistical modelling, have given soil scientists the tools

to capture multiple physical and chemical properties at once, reducing the reliance on hazardous reagents and moving toward a 'green chemistry' approach with reduced plastics and hazardous waste in routine soil labs.

Other non-chemical methods include passive samplers (**Figure 1**), which can mimic diffusion of nutrients from the soil matrix into a solution, and are a promising alternative to chemical extractions for measuring concentrations of diffuse pollutants from soil into water. Passive sampling using diffuse gradient thin films and coated FeO strips work on the fundamental soil principle that was uncovered in the 1850s, i.e., nutrients can diffuse from the soil matrix, into the soil solution and are taken up by plant roots. So as chemical methods of soil analysis incorporate advanced techniques, the principles on which they are founded can be rooted in very early discoveries from the 1800s.

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