

Soil Science and Technology
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Lecture - 55
PXRF Soil Applications

Welcome friends to this fifth lecture of week 11 of Soil Science and Technology. And in this lecture, we will be talking about another advanced sensor and its application for soil measurement and this sensor is called PXRF or portable X-ray fluorescence. So, this portable X-ray fluorescence is an advanced radioactive sensor where it you know where energy released by replacing of inertial electrons by outer shell electrons termed fluorescence is quantified by a silicon drift detector in the aperture of the instruments.

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PXRF

- Energy released by replacing of inner shell electrons by outer shell electrons (termed fluorescence) is quantified by a silicon drift detector in the aperture of the instrument.
- Scanning (dwell) time for a given sample is typically ~60-90 s.
- **Advantages:**
 - Field portability
 - No consumables
 - Non-destructive
 - Multi-elemental analysis (providing simultaneous analysis of ~20-30 elements)
- **Parameters:**
 - Soil pH, EC, CEC, P, K, Ca, Mg, S, Micronutrients, Gypsum, %BS, Heavy metals, permafrost pH, LULC, Parent material, Profile horizonation, Geochemistry, Compost EC, Compost CEC, Water heavy metals, Leaf

The slide also includes a diagram of an atom showing electron shells (K, L, M, N) and energy levels, and a diagram of the PXRF instrument's internal components including the X-ray source, detector, and sample holder. A photograph of the handheld PXRF device is also shown.

So, I will discuss this in details and scanning time for a given sample is typically varies from 60 to 90 seconds. So, this is the instrument it is basically gun shaped instrument, you can literally take it into the field directly and you can measure it. You can touch it into the soil surface and then you can pull that trigger and it will give you reading of. Thus you know 20 to 30 elements simultaneously directly here in the screen and in the ppm level; so, within 60 to 90 seconds. So, this is called portable X-ray fluorescence.

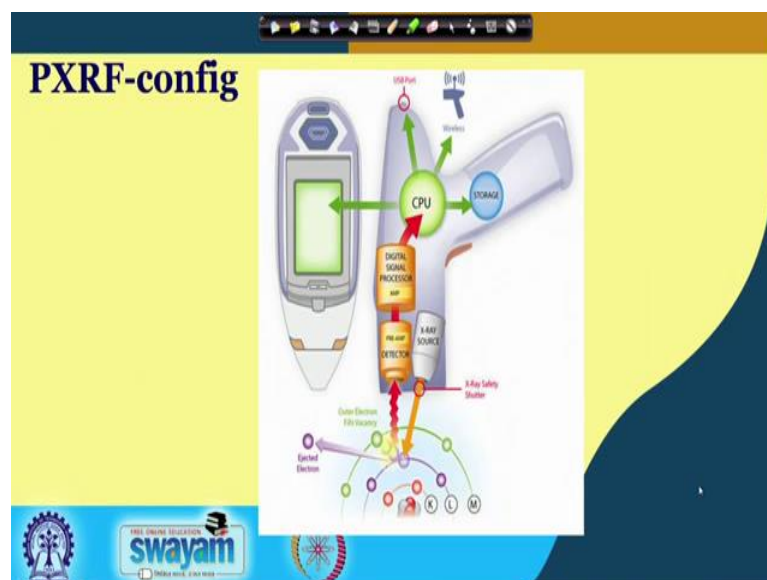
Now, what is the advantage of this technology? First of all, it is field portable. It requires no consumables, you can directly go to the field and you can touch the surface. You

touch this instrument to the soil surface and you can pull the trigger and it will give you directly the total elemental measurements. It is non destructive. So, even you are not supposed to do any type of you know it does not destroy the soil. So, you can use it for later use also and also you can do the multi elemental analysis like providing simultaneous analysis for 20 to 30 elements.

So, you can use this technology for getting simultaneous quantification values for 20 to 30 elements. So, what are the parameters you can generally you can measure through this instrument? You can measure a wide range of parameters starting from soil pH, you know EC, Cation Exchange Capacity, phosphorus, potassium, calcium, magnesium, sulfur, micronutrient, gypsum, percent by saturation, heavy metals permafrost pH, land use land cover, parent material, profile horizonation, geochemistry, compost electrical conductivity and compost cation exchange capacity, water heavy metals and leaf elements so on so forth.

So, you can see we can use this technology for measurement of a wide range of soil properties which you know which would take a long time to measure with a standard method of soil standard measurement protocol.

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So, if you see the internal configuration of this PXRF; you will see here, there is an you know first there is an x-ray source which generates basically x-rays. So, these x-ray basically hits the electrons which are present in different orbitals and these energy by

taking these energy these electron ejects from there and goes to higher orbitals. And after going to the higher orbitals, it will reach back revert back to the original position and while reverting back to its original position it releases some amount of energy. And this energy is called the fluorescence energy.

Remember that these fluorescence energy is a characteristic feature for each and every element. So, each and every element will release fluorescence energy at different wave length or different you know different x-ray I would say different values of X ray energy. So, these wavelength or these fluorescence will be detected by a detector which is present inside this instrument and then it will produce and then it will be go to a digital signal processor and ultimately to the CPU which will further analyze and display the results here.

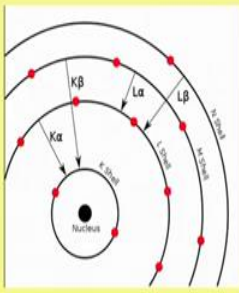
So, this is how this instruments works and there is an USB port from which you can take out the results or you can directly you know you know use the Bluetooth also to produce to save it to other computers also and you can run it through lithium ion battery. So, you know the lithium ion batteries can be chargeable and you can use it for on site say onsite scanning also. So, on site you know on site measurement. And also nowadays these instruments are having these you know integrated cameras which can take the photographs of this also while you are taking the measurement of you know it can take the images of the soil when you are taking the images when you taking the scan.

So, guys let us go ahead and see what is the principle of working.

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PXRF-config

- Each element has electronic orbitals of characteristic energy
- Following removal of an inner electron by an energetic photon provided by a primary radiation source, an electron from an outer shell drops into its place
- There are a limited number of ways in which this can happen:
 - L→K transition is traditionally called $K\alpha$
 - M→K transition is called $K\beta$
 - M→L transition is called $L\alpha$
- Each of these transitions yields a fluorescent photon with a characteristic energy equal to the difference in energy of the initial and final orbital
- The wavelength of this fluorescent radiation can be calculated from Planck's Law: $E = nh\nu$
 - $n=1,2,3,\dots$; h = Planck's constant; ν = frequency
- The fluorescent radiation can be analyzed either by sorting the energies of the photons (energy-dispersive analysis) or by separating the wavelengths of the radiation (wavelength-dispersive analysis)
 - Intensity of each characteristic radiation is directly related to the amount of each element in the material



The diagram shows a central nucleus with concentric circles representing electron shells labeled K, L, M, and N. Red dots representing electrons are placed on these shells. Arrows indicate transitions: $K\alpha$ from L to K, $K\beta$ from M to K, $L\alpha$ from M to L, and $L\beta$ from N to L.

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So, basically when a electron I mean when a x-ray, you can see that any element it contains a nucleus and there are several orbitals and in this orbitals different element you know electrons are present and these are the electrons is red buttons are the electrons. So, this is a K shell, L shell M shell and N shell. So, when the electrons you know these electrons are energized by some extra energy, these electrons gets ejected and goes to the higher orbitals and energize and go to the higher orbitals. And after a certain period of time it will revert back and cascade down to their original position.

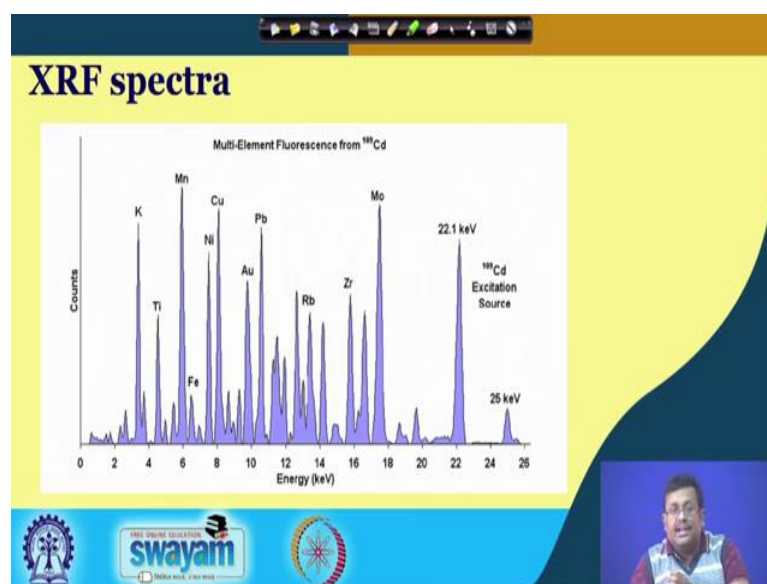
So, while cascading down to the original position, they will remove some energy; they will release some energy in the terms of fluorescence and these transition can occur through a limited number of ways. For example, when a move when a movement of electrons from energize higher energy orbital to lower energy orbital occurs from L shell to K shell, we call it $K\alpha$. And then you know when from M to K shell, M shell to K shell, it is called $K\beta$ and similarly from M shell to L shell, it is called $L\alpha$, then N shell to L shell that is called $L\beta$.

So, you see these are the different types of transitions. So, each of these transition yields a fluorescent photon with a characteristics energy equal to the difference in energy of this initial and final orbital. And the wavelength of this fluorescence radiation can be calculated from the Planck's law. You know the Planck's law says that $E = nh\nu$ where h is the ν is the Plancks constant and ν = frequency. So, the fluorescent radiation can be

analyzed either by sorting the energies of the photons or by separating the wavelengths of the radiation.

So, when they are using this by; when they are analyze either by sorting the energies of the photons, we call it energy dispersive analysis. And when they are separating by wavelengths of the radiation, then we call wavelength dispersive analysis. And remember these portable XRF or this or this handheld XRF is basically if an variant of this energy dispersive x-ray fluorescence analysis. So, intensity of each characteristic radiation is directly related to the amount of each element in the material.

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So, in the next slide it will be much more clear. So, you can see this is the energy of the x-ray varies from 0 to 26 kilo electron volt. Now and you can see these are the individual peaks which are arise which arose due to the transition due to the you know due to the transition of the electrons. So, these peaks generally arise at certain you know energy levels. And for example, this is a K peaks, this is a Ti peaks, this an Mn peaks and; obviously, the height of the peaks is related to the concentration of that particular element.

So, once this so, these instrument basically captures this peaks. And once it captures these peaks it got an internal factory calibrated standard using what it directly you know predict or directly gives the quantified values of each of the elements. Remember that these instrument gives you basically the total elemental concentration.

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PXRF basics

- A battery operated, Olympus Vanta series PXRF (Rh X-ray tube operated at 10-40 kV)
- Internal calibration based on known energy emission
- Silicon drift detector for light element analysis
- Instrument operated in *Geochem mode*
 - Uses a scatter normalization algorithm (per EPA Method 6200) for soil, liquids, and powders allowing for sequential analysis of atomic numbers Z=15 (Phosphorus) to Z=92 (Uranium)
 - Optimized tube excitation increases performance on lighter elements (Ca, K, S, P, Cl, and I)
- Samples scanned for 30 s per beam through the ~2 cm aperture
 - One complete scan in 60-90 sec.
 - Can be used on soil, vegetation, water matrices

Allows for multiple soil science applications:

- Heavy metal assessment
- Gypsum/calcic/podzol horizons
- Soil fertility (CEC)
- Soil pH/EC

Logos: Swamyam, Ministry of Education, Government of India

So, this is basically battery operated this an model Vanta which is one of the advanced model produced by Olympus company. And this is this x-ray, this contains a rhodium x-ray tube which operated at 10 to 40 kilo electron volt and then the internal calibration based on known energy emission and obviously, it has got a silicon drift detector for light elemental analysis.

And remember that you can use this instrument in different modes. You can use it in Geochem modes or sometimes there has an instrument, which you can use in soil mode also. So, basically it uses a scatter normalization algorithm in Geochem mode for soil liquid and powders and it allows the sequential analysis of atomic numbers starting from phosphorus to uranium. So, it can measure anything starting from phosphorus to uranium, there are some also instrument which can measure magnesium to uranium. That means atomic number of 12 to uranium.

So; obviously, there are the it has got two beams you know basically; so, two to three beams. So, each beam takes 30 seconds time. So, the total scanning time for one sample is around 60 to 90 seconds and you can use this instrument for multiple soil science applications like heavy metal assessment like gypsum, calsic, podzol horizonation, then soil fertility measurement or CEC, then soil pH and EC measurement and so and so forth.

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And this basically shows the limit of detection of different elements using this instrument. So, you can see here load obviously, this color are showing different different limit of detection. And; obviously, it is visible that for most of the elements. These instruments have a limit of detection of less than 5 ppm. So; that means, if the instrument have if the concentration of that particular element in the environment is 5 ppm or less than that, this instrument can measure it. And also these are some other ranges like 10 ppm, you can see here and also so you know however it cannot measure hydrogen, lithium, beryllium and sodium and these you know gray point like you know carbon and nitrogen.

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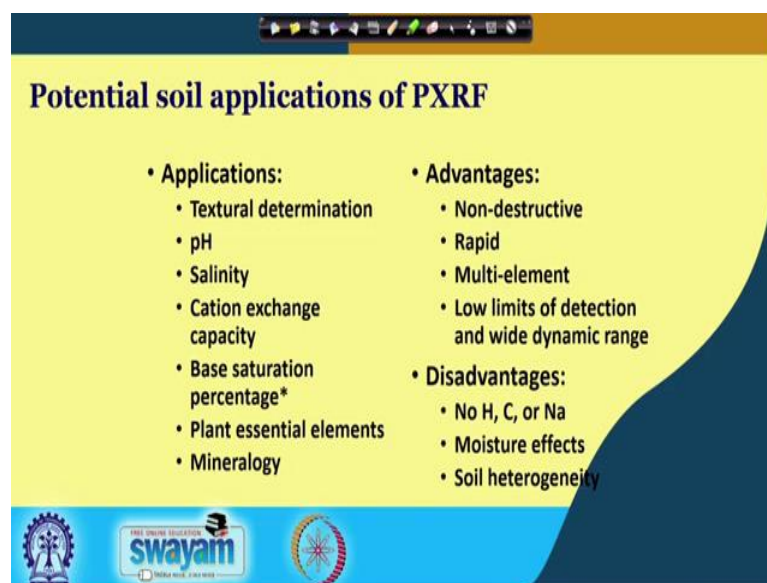


So, what are the reference methods? So, nowadays these instrument has been considered as a reference method for soil analysis and there are three reference method which are available. First of all the US-EPA method or United State if environmental protection agency method 6200 which is available for which is a reference method.

Then USDA United State Department of Agriculture NRCS method where it considered as a important method for soil measurement. Another method is published by myself and Dr. David C Weindorf which is professor of Texas Tech University and right now it is considered as a official method by Soil Science Society of America which is the another one of the most important society of soil science across the world.

So, these are some reference method so; that means, these instrument nowadays considered as an important method for soil analysis.

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Potential soil applications of PXRF

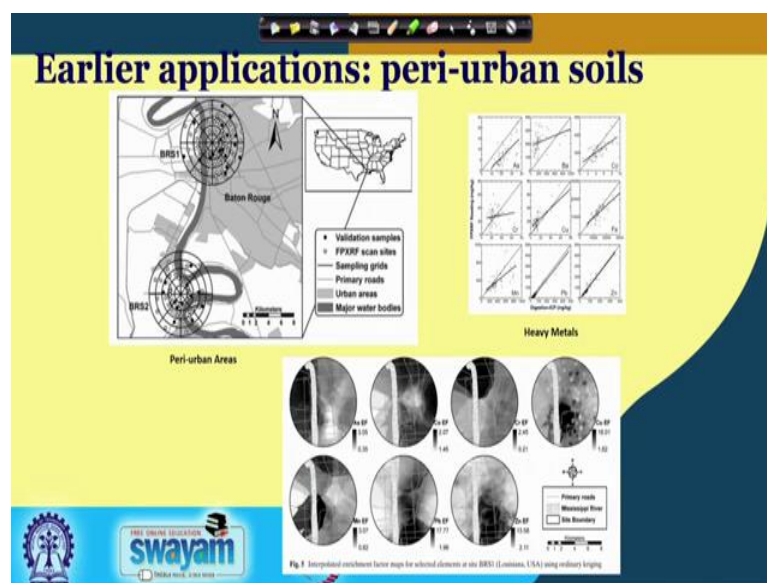
<ul style="list-style-type: none">• Applications:<ul style="list-style-type: none">• Textural determination• pH• Salinity• Cation exchange capacity• Base saturation percentage*• Plant essential elements• Mineralogy	<ul style="list-style-type: none">• Advantages:<ul style="list-style-type: none">• Non-destructive• Rapid• Multi-element• Low limits of detection and wide dynamic range• Disadvantages:<ul style="list-style-type: none">• No H, C, or Na• Moisture effects• Soil heterogeneity
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The slide features a yellow background with a blue header and footer. The title 'Potential soil applications of PXRF' is in bold black text. The content is organized into two columns. The left column lists applications, and the right column lists advantages and disadvantages. The footer includes the Swamyam logo and the text 'FREE ONLINE EDUCATION swamyam'.

So, application potential soil application for PXRF; obviously, the application varies from textural determination, then pH, then salinity, then cation, exchange capacity, then base saturation percentage, plant essential elements mineralogy. And all these you can measure what are the advantages; obviously, this is a non destructive. As I have already told you, it is rapid only 60 to 90 seconds, you require. It is multi element you are getting multi elemental results.

It is lower limit of detection and wide dynamic range you are getting. Disadvantage; obviously, it has got several disadvantage. First of all it cannot measure hydrogen, carbon and sodium and it has got some influence of moisture effect. So, when the moisture content of the soil goes beyond 20 percent it, it interfere with the results and also soil heterogeneity because when the soil is highly heterogeneous. So, it has got a very small aperture through which it can measure. So, you need to take multiple measurement and then average to get a average value of soil parameters. Otherwise the soil is very very heterogeneous in nature.

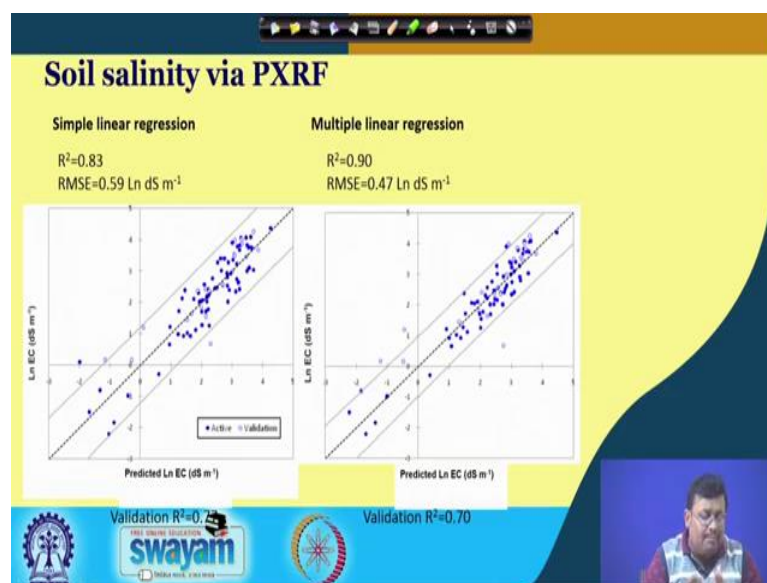
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So, let us talk about several application of this method. So, 10 years back we started this we started this application of this instrument for measuring the heavy metal contents in Peri-urban soils and you can see here. We went to the field and we collected several samples from the peri-urban agricultural areas of United States. And after bringing the samples into the lab, we measure these heavy metal [elemental/elements] elements like arsenic, barium and then arsenic, the barium then, cobalt, then chromium, copper and then iron manganese lead and zinc.

And we saw there is a good correlation between our heavy metals and this PXRF reading. So, we measure this heavy metals in the land using standard ICP or method and there we correlated using our handheld PXRF method. So, we got good correlation and based on this correlation we develop certain models and we also produce some spatial variability maps for this area for this individual you know for this individual elements. So, that first shows the use of this technology for you know rapid measurement and mapping of soil heavy metal.

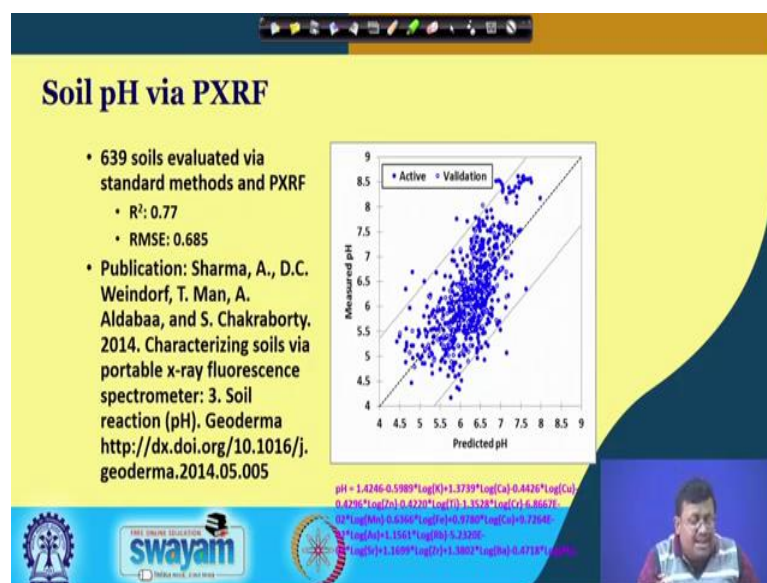
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Also you can see we have use this for rapid measurement of soil salinity. Soil salinity is an important parameter and you can see we have proved that use this technology, you can predict the soil salinity using simple linear regression or multiple linear regression. In the simple linear regression, we are using 0; we are getting an R^2 values of 0.83 whereas, in multiple linear regression we are getting 0.90. So, basically we are using these elemental content. We are getting several elements starting from starting from magnesium to uranium.

So, using selected suit of elements we are using them as a proxy it or measurement of for measurement of particular you know for measurement of particular soil property. In this case it is electrical conductivity or salinity and we are getting very good result. So, that proves that this instrument can be used for predicting soil salinity.

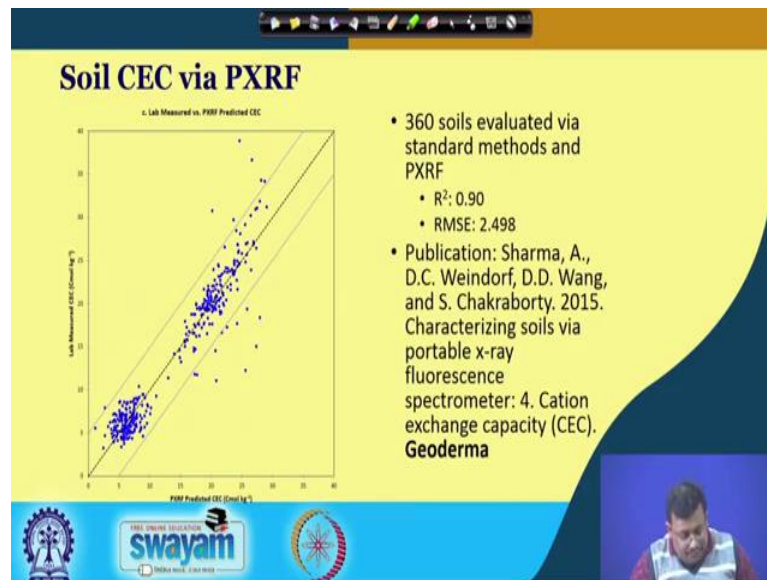
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Not only that you can predict soil pH using this PXRF because soil pH we have you know soil pH can be of you know soil pH is basically influenced by several elements. For example, in the low pH soil, you see the soil iron as well as soil you know the concentration of iron and manganese is high. Whereas in high pH soil or calcareous soil, you will see that calcium content is high and all these elements can be measured through this PXRF.

So, basically we use this elements along with other elements as a proxy for measurement of soil pH and we got an R^2 values of 0.77. So, that shows that these elements can be used to predict the soil pH reasonably with an good R square values of 0.77.

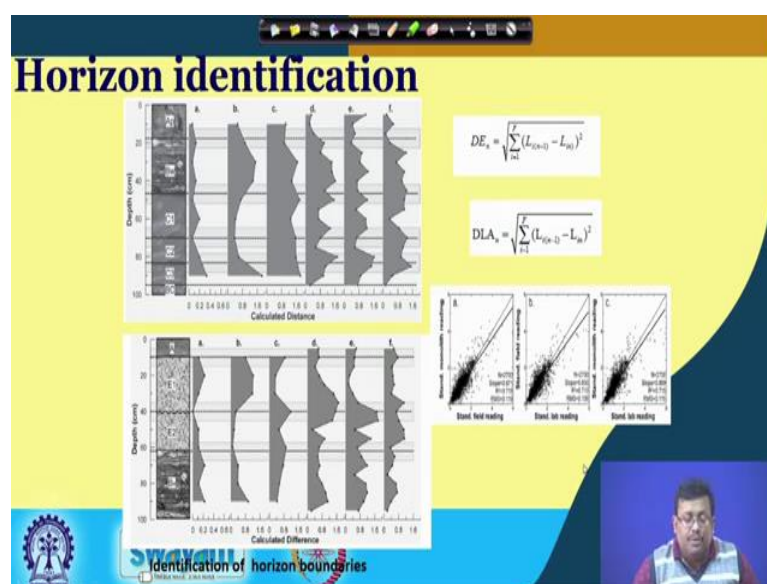
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And also we predict the soil CEC or cation exchange capacity which is an important fertility parameter.

So, we collected three hundred sixty soils and we predict the soil CEC by using this sample element values and we got an R^2 of 0.90 and obviously, it was you know it was a you know very good result and it was published in the journal Geoderma. So, you can consult this paper which is published in journal Geoderma.

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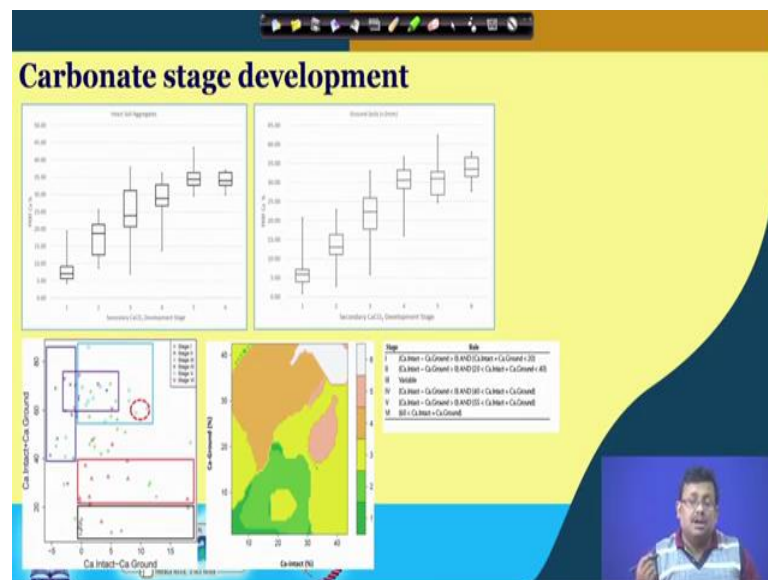


And also we have proved that these PXRF can be useful for identification of the horizon in the soil profile.

So, in the soil profile if you remember in the soil classification lecture, we talked about how we horizon how we define different horizons or also we discussed that in the soil survey lecture also. So, pedology is using there you know morphology using morphological features after digging a feet in the field and using some morphological differences, they calculate and they make you know qualitative differences between these different horizons. And from there they defined different horizons O horizon, A horizon, B horizon.

However, we use this PXRF for getting a quantitative we to give a quantitative estimation of this horizon differentiation and we developed a index. And using this index we developed a precise plan through which we can differentiate or we can precisely identify this horizon transition boundary. So, that was also an application for soil science and pedology for pedology.

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So, also you can see in the soil there is several degrees of carbonate development. There are 6 different degrees of carbonate development and we have proved by using this technology, you can predict the carbonate development stage in the field itself.

So, we have proved we have produced some you know rule based algorithm and using this rule, you can predict which is the practical which is the actual you know carbonate development stage in the soil. So, you can see you know you know this technology can be also be used for extensive use in you know extensively used in pedological parameters.

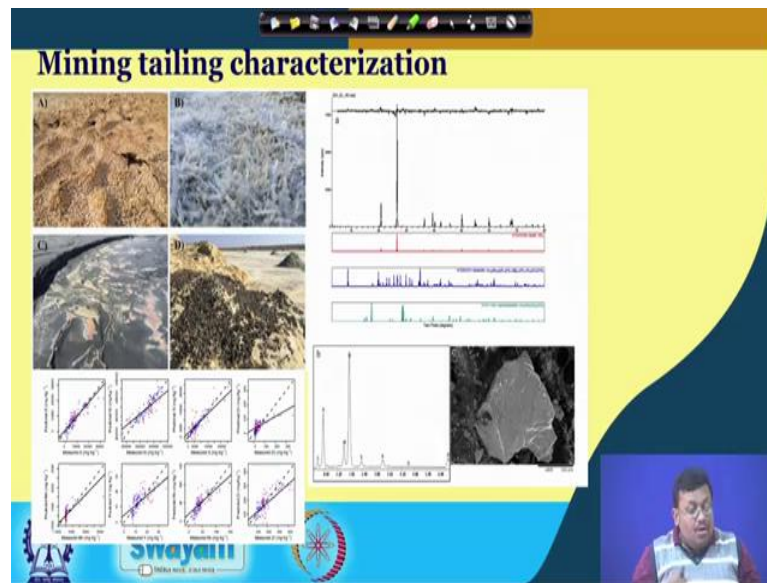
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Now, heavy metals in European soil in the this study was conducted in Romania and you see we went to the field and we collected several soil samples from different areas. And after collecting the soil samples, we predicted their concentration using geostatistical interpolation.

You can see we are producing the map of chromium, then copper, then zinc, then arsenic and lead and not only that we also divides the area into contaminated, uncontaminated, moderately contaminated and moderately strongly contaminated areas on the basis of geo index of geo accumulation. So, we collect we calculated the index of geo accumulation and also we divided or we demarcated different areas which are you know highly contaminated area. So, using this technology, it is possible to rapidly identify and map the highly contaminated areas in the field itself.

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We also use this technology for mine tailing characterization. So, we collected samples from four different mining sites in South Africa and we use this technology to predict different elements, which is present in that mining tailing mine tailing soils. We got a very good correlation between our results and standard measure. So that means, we can use this technology for rapidly measuring the elemental content in mining soils also.

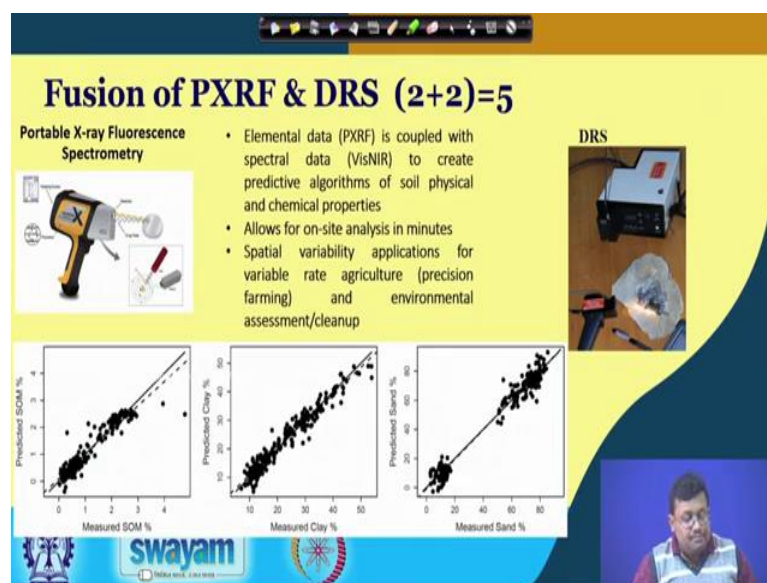
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Not only that we can also use this technology for identification of the parent material. You know the parent material is a very important thing as you know and also shows how

the also shows the genesis of the soil from which the soil actually for which soil actually produce. So, you have produced that we have proved that these technology can also be used for predicting the soil parent material and different type of parent material like you can see. Not only the predicting the parent material, but we can also map it directly into the field.

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So, right now we have whatever we have discuss is basically the application of PXRF and DRS and you know we have shown there I have discuss their application in vary in varying you know; so, in measurement of vary you know to wide range of soil properties. So, we measure the organic carbons, sand, silt, clay and then should and then nitrogen and then all these things using DRS. And this PXRF can be used specially for measurement of elemental content in heavy metals.

So, you see there are have being you know there is a kind of complementarity between these two. Organic carbon cannot be measured through PXRF; however, these DRS can measure the organic carbon whereas, these elemental content does not have elements or heavy metal does not have any direct spectral features in the DRS spectra; however, we can measure them directly using their PXRF. So, you can see both of them these technologies are complementary to each other. So, lately we have seen that if we combine the data set together; that means, we are getting the spectra from DRS and we are getting the elemental values from the PXRF.

So, if we combine them together and we use them together as predictor in any type of prediction models will get better results which will produce it will show us better results than either of these instrument. So, basically we will be getting a synergistic results where will be getting 2 plus 2 equal to 5. So, you see here elemental data is coupled with spectral data to create predictive algorithm of soil physical and chemical properties and this allows us to onsite analysis in minutes and spatial variability application for variable rate agriculture you know agriculture farming or precision farming you can do.

So, you can see here three different parameters, we have measured here. Soil organic matter percentage, clay percentage and sand percentage you can see. All of them are following this 1 is to 1 line very closely. So, that shows if we combine this technology together, it will show us better results. So, nowadays that is an extensive focus on these combined technology research. So, those who wants to do further research and advanced research in this area, they can do this research in the combined sensor fusion we call it sensor fusion.

Now, sensor fusion is now a very very hot topic and you can use this sensor fusion to measure a wide range of soil particles or wide range of soil properties on site. And you know there has you know you can develop some new sensor which will combine these two you know these two and you can develop say new prototype where you can combine these two technologies together and then you can fit it with any tractor. So, that these tractor moves that it will directly feed the information or it will directly scan while this tractor is moving and it will be produce and it will predict or you know one side and produce directly the map of spatial variability of soil properties.

So, guys while try to show you couple of examples of advanced uses of this sensors. Obviously, you know it is not possible to discuss in details about this technologies because it requires a huge amount of study. But I hope that you have learned about something new thing, which is not covered in traditional courses of soils and there are certain other also advanced sensors like you know optical sensors are developed nowadays in different advanced countries and also in India which we can use for non destructive measurement of soil properties.

So, please focus on these because these are the future of soil science. You know a time will come that the traditional soil analysis has to be replaced by this dry chemistry

measurement because the time and consumable and the cost involvement in the traditional methods is cannot simply catered the need for a huge farming community like in India. So, we have to think about some alternative. Obviously, we are not nullifying the standard method because these are accurate methods, but this has to be supported by these you know alternative and low cost and noninvasive methods.

So, you can go ahead and you can do some more study and you can do some more defined research. Obviously, there are plenty of literature is available for detailing these technologies. So, I will encourage you to go ahead and you know see some literature for these technologies and then you can do your own research.

So, guys we have you know let me wrap up this week 11 here and hope you have got some you know overview of knowledge you know knowledge overview for some advanced sensors and advanced technologies nowadays we are utilizing in the field of soil science. And hopefully this will be helpful in your respective research areas also. And so, let us meet in week twelve with a new topic that is digital soil mapping.

Thank you.