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Lecture – 59 Analytical Techniques for Assessing Soil Pollution Continued

Welcome to this fourth lecture of week 12 or module 12 of this NPTEL online certification course of environmental soil chemistry, and in this week, we are talking about different analytical methods for assessing soil pollution and in the previous 3 lectures we have talked about different types of instruments or methods which we use for analysis of different inorganic pollutants in the soil.

We started with nitrogen and we also talked about talked about phosphorus. So, in today's lecture we will be talking about basically salts, then we will be talking about trace elements and other elements, total elemental analysis and then will be moving towards the organic pollutants.

(Refer Slide Time: 01:06)

Determination of inorganic pollutants

Analytical methods for Salts

- The accumulation of soluble salts in the soil profile obstructs crop growth by increasing the osmotic potential of the soil solution and inducing specific ion toxicities or nutrient imbalances
- The principal cations: sodium, calcium and magnesium
- The principal anions: sulphate and chloride
- Minor amounts of potassium, bicarbonate, carbonate and nitrate ions may also be present.
- High concentrations of sodium at cation-exchange sites disperse solids and impede water and air movement

So, let us start today with the analytical methods for salts in the soil. Now you know that accumulation of soluble salts in soil profile obstructs crop growth by increasing the osmotic potential of the soil solution and inducing specific ion toxicities or nutrient imbalance. So, the salty soils, I mean the soils which shows high salinity are not suitable for plant growth and there are several salts which are mainly responsible for soil salinity.

But the principal cations are basically sodium and then calcium and also magnesium. And as far as the principal anions are concerned, the principal anions are mainly sulphates and chlorides. Apart from that, some minor amounts of potassium, bicarbonates, carbonates and nitrate ions also may be present. Now high concentration of sodium at cation exchange site disperses the solids and impedes water and air movement.

And as a result of that there is a crust formation at the soil surface. And the sodium saturated soils are not physically beneficial for the growth of the crop that why we generally go for different types of treatment to reclaim the soil salinity. So high concentration of sodium at cation-exchange sites always is harmful as far as the soil physiochemical properties are concerned.

(Refer Slide Time: 02:51)



Now there are mainly 2 methods which we use for measurement of salt concentration in the soil, one is through electrical conductivity meter or EC meter or the second process or second method is electromagnetic induction method. So we are going to discuss both of them. (Refer Slide Time: 03:12)

Determination of inorganic pollutants Analytical methods for Salts EC meter Measures the electrical conductivity in a solution Electric Conductivity depends on: Concentration of ions (higher concentration, higher Electrical Conductivity): Since each ion has its own specific ability to conduct current, Electrical Conductivity is only an estimate of the total ion concentration. Temperature of the solution (higher temperature, higher Electrical Conductivity); The Conductivity of a solution is highly temperature dependent, therefore it is important to either use a temperature compensated instrument, or calibrate the instrument at the same temperature as the solution being measured. Specific nature of the ions (higher specific ability and higher valence, higher electric conductivity)

So, let us start with the EC meter or electrical conductivity meter. Now, this EC meter is an instrument which basically measures the electrical conductivity in a solution. Now this electrical conductivity depends on several factors. The first factor is concentration of ion. Obviously, this higher concentration of the ion obviously goes with the higher electrical conductivity.

Since each ion has its own specific ability to conduct current, electrical conductivity is only an estimate of the total ion concentration. Now you might ask me why we go for the electrical conductance measurement while we measure the salt concentration. Now salts are basically composed of different types of cations and anions and these cations and anions are known for conducting the current.

So that is why while measuring the electrical conductivity, then we can have an idea about the soil concentration. So concentration of ions as I have mentioned that each ion has its own specific ability to conduct current, electrical conductivity is only the estimate of total ion concentration. Now the second important factor is the temperature of the solution. Remember that higher the temperature, higher the electrical conductivity.

Now the conductivity of a solution is highly temperature dependent remember, therefore it is important to either use a temperature compensated instrument which can automatically calculate the temperature compensation or the changes in temperature and based on that it can compensate the reading or calibrate the instrument at the same temperature as the solution being measured.

So, there are several ways to take care of this temperature variation. The third important factor is the specific nature of the ions that means higher the specific ability and higher valency, higher will be electrical conductivity. So you can see that electrical conductivity depends on several factors.

(Refer Slide Time: 05:10)



Now this EC meter, the basic principle of this EC meter. As you can see this is an EC meter, so there is an electrode and in this EC meter basically the principle says that that 2 plates are placed in a sample and a potential is applied across the plates which is basically normally a sine wave voltage and the resulting current is being measured. So electrical conductivity is generally denoted by the symbol sigma and its SI unit is Siemens per meter.

Generally, it is called Siemens per meter okay or sometime we call it deci Siemens per meter also. So Siemens per meter or deci Siemens per meter is there in SI unit. Now reverse of electrical conductivity is known as the electrical resistivity. Remember the reverse of conductivity is resistivity which is denoted by a symbol rho that is this symbol, rho symbol and so remember that there is a relationship between the potential that is we denote the potential by V and current by I.

So there is a relationship between the potential V and current I which is given by the Ohm's law. Now according to Ohm's law, the current increases with the increase in potential. So you can see the current increase with the increase in potential means the current is proportionate

to the voltage, I am sorry the current is proportional to the potential V. So V varies as I. So you can write V = RI.

Where this R is a proportionality constant, we call it a resistance or in other words R = V by I. So resistance also depends on the temperature and increase in temperature decreases the resistance. So that is why there is a profound influence of temperature in measuring the electrical conductivity and this is how we measure the electrical conductivity in the lab. Generally in the lab, we use the electrical conductivity meter to measure the conductivity of the soil water solution.

And we can prepare the soil water solution, we can measure the electrical conductivity in different ways. We can either make a soil water solution with a fixed ratio of 1 is to 2 or we can make a saturated paste. Saturated paste mean we saturate the soil with the water and keep it overnight and the next day we measure the electrical conductivity of that paste directly inserting the electrode into that paste.

Another way is to extract the saturation extract. Saturation extract basically is done by the help of a vacuum pump as well as Buchner funnel and the saturation extract also by extracting the solution or saturation extract, we can also measure the electrical conductivity. So, there are different ways of measurement of electrical conductivity, however we all measure them using this electrical conductivity meter.

(Refer Slide Time: 08:52)



So let us move ahead and see the next important thing that is electromagnetic induction. Now, the electromagnetic induction was discovered by Michael Faraday in 1831 and James Clerk Maxwell, he mathematically described it as a Faraday's law of induction. So the exact law says that the electromotive force around a closed path is equal to the negative of the time rate of change of the magnetic flux enclosed by the path.

So in simplified form, this could be achieved when a conductor is placed in a moving magnetic field, so this situation can arise when we place a conductor in a moving magnetic field, for example when using AC power source or when a conductor is constantly moving in a stationary magnetic field. So, there are 2 ways which through which we can realize this Faraday's law of electromagnetic induction.

(Refer Slide Time: 10:08)



So, let us see in the next slide. So in the next slide for example in this picture you can see that this electromagnetic induction can be achieved when a magnet, so suppose this is a magnet, so this magnet and a wire, so using this magnet and wire we can create the electromagnetic induction, how? So when a magnet and wire move relative to each other, a voltage is induced according to this Faraday's law of electromagnetic induction.

So, when we move these two with relative to each other, then a voltage is developed or induced. So, this amount of voltage produced depends on 3 things. First of all speed through which we can move these two thing that is magnet or this wire, that is one of the major importance. So, the high speed produces the high voltage. Second is the magnetism, so strong magnets produce high voltage.

And third is shape of the wire that means you can see as we are increasing the number of coils in the wire that will produce increasingly higher voltage. So, you can see here there are 2 things here, one is electrical field, so electrical conducting wire here, and there is a magnet. So if we move the magnet through this coil, there will be a current generation or voltage generation.

So production of this voltage is depends on the speed through which we move this magnet secondly the stronger is the magnet produce strong voltage and thirdly if we increase the number of coil then we can get the more higher voltage.

(Refer Slide Time: 11:54)

Determination of inorganic pollutants

Analytical methods for Salts

- Electromagnetic Induction
- The electromagnetic (EM) induction method is based on the measurement of the change in mutual impedance between a pair of coils on or above the earth's surface. Most EM instruments are comprised of two or more sets of coils.



So how we use this principle in actual measurement of soil concentration. So let us see this. So basically, this EM sensor or electromagnetic induction method is basically utilized in this EM sensor for soil science. So, this electromagnetic induction method is based on the measurement of the change of mutual impedance between a pair of coil on or above the earth's surface.

So basically through this instrument, this you can see here this is an electromagnetic induction instrument, so through this instrument we can measure the change of mutual impedance between a pair of coil, so there is a pair of coil, so you can see here there is one pair and this is a pair of coil, this is the first coil and this is the second coil. So, the first coil is known as the transmitting coil and the second coil is known as the receiver coil and they are separated by fixed distance.

So, in this electromagnetic or EM sensor, there are 2 coils which are separated by a fixed distance, one is transmitting coil, another is receiver coil. So basically, we apply this EM method by measuring the change of impedance between a pair of coil on or above the earth's surface. How we will see and most of the EM instruments are comprised of two or more set of coils we can see here.

(Refer Slide Time: 13:25)



Now, these coils are electrically connected. So these 2 coils are basically electrically connected as you can see and they are separated by a fixed distance. Now this transmitter coil basically is used to generate an electromagnetic field at a specific frequency. So basically it first generates a current, we will call it C1 and this current C1 induces a magnetic field. Why it induces a magnetic field? Because remember earth acts as a big magnet.

So when we move these coils with respect to the earth's magnet, obviously there will be an electromagnetic induction. So this transmitter coil produces a current one, this current one induces a magnetic field M1 and this M1 induces C2, so C2 is basically a secondary current. So this M1 induces a C2 in the subsurface and or on object of the surface. So C2 further induces a second magnetic field that is called M2 and M2 further induces C3 in the receiver.

So you can see here this first coil a transmitter coil produces a current C1 which induces a magnetic field M1. This magnetic field basically induces a current called eddy current which is denoted by C2 in the subsurface and then C2 induces M2 in the vicinity of the receiver coil

and this M2 or secondary magnetic field produces another current that is C3 in the receiver. So this is how this total flow of this electromagnetic induction goes on.

Now remember that the transmitter coil, basically as I have told you the transmitter coil is used to generate an electromagnetic field at a specific frequency and this is known as the primary field. So you can see here this is the primary field. So the primary field causes electrical current to flow in conductive material, so earth is a conductive material, so flow in the conductive material in the subsurface, the flow of the current in the subsurface we know.

And this is called the eddy current generates a secondary magnetic field M2 which we have already discussed and which is sensed by the receiver coil at the end. Now remember that the magnitude of the secondary field sensed by this receiver depends upon the type of distribution of conductive material in the subsurface. So, in the earth, what are those conductive materials?

The salts are the conducting materials because they are basically dissociated in the ions. So, these ions are the conducting materials. So this flow of current is basically mediated by the ions of the salts which are present in the subsurface. So depending on the concentration of the salts, depending on the composition of the salts, the magnitude of the secondary field sensed by the receiver varies.

So both induced and secondary field along with the primary field are detected at the receivers end or receiver coil. So, this is how when you move this EM instrument with respect to the soil surface, this primary, this coil one or transmitter coil basically creates an electromagnetic induction and this electromagnetic induction is helping a flow of current through the salt solution, through the salt ions which are basically conducting materials.

And this current produces the secondary magnetic field which is basically sensed by the receiver coil, and this is how depending on the concentration or depending on the composition, we can see the variation of the salt concentration. So, this is how this electromagnetic induction method basically works in the soil science discipline.

(Refer Slide Time: 17:56)



Now let me show you a picture. So basically you can see two points, one is the electromagnetic induction which is inducing voltage by changing the magnetic field around a conductor and secondly the important thing is any change in the magnetic field will induce a voltage. So if we move this EM sensor with respect to the earth's magnetic field that will induce a voltage which will be measured at the receiver coil. So, this is how we measure the salt concentration in the soil.

(Refer Slide Time: 18:32)



This is actually the instruments you can see. Basically, the researcher or the scientist has to move this bar, you can see the bar. So, there are two sensors at the two ends, two coils and two ends and you can see when it moves with respect to that surface then there will be creation of or induction of voltage. So, this is how this electromagnetic induction is basically measured in the soil.

(Refer Slide Time: 19:04)

Determination of inorganic pollutants

Analytical methods for trace elements

Trace elements in soil frequently analyzed: Cd, Cr, Pb, Cu, Ni and Mn

Type of analysis	Role
Total	baseline; essential and polluting elements
Pseudo total	heavy metal and other pollutant contents
Extractable	mobile or plant-available contents
Speciation	element form, phase, compound, oxidation state

So we have completed the soil. The next let us talk about the analytical methods for trace elements. Now the trace elements in the soil frequently analyzed are cadmium, chromium, lead, copper, nickel and manganese. Apart from that there are some metalloids also, most importantly arsenic is also measured by different methods. And there are certain methods which can measure most of the elements in the earth's crust.

So depending on the type of analysis, there are different types of naming. For example the total analysis, the total analysis is basically the baseline analysis and it is essential for all the pollutant elements. So essential and pollutant elements we need the total analysis. For example if we are interested to measure the lead concentration or lead contamination in the soil, we should go with the total elemental analysis.

So total elemental analysis can also be done by different way. So total elemental analysis for that you need to use certain kind of digestive material or digestion mixture. For example hydrofluoric acid. And apart from this total analysis, you can go with the pseudo total analysis also. So pseudo total analysis helps for the heavy metal and other pollutant contents also sometimes.

Then there is an extractable element also, which basically denotes mobile and plant-available contents and speciation also which element form, phase, compounds, oxidation states. So you can see depending on whichever form you want, you can use different types of reagents to extract that form. For total analysis you have to use different extraction. For pseudo total analysis you have to use different types of extraction.

For extractable or mobile you have to use different types of extraction and so on so forth. So, this is how based on our desired output or based on our specific element, we go with the specific type of analysis.

(Refer Slide Time: 21:20)



Now there is no scope to discuss about different types of extracting reagents for each of these elements, however, I am going to talk about the important analytical techniques or analytical methods which you use for measurement of the trace elements or different other elements also. So let us talk about the atomic absorption spectroscopy. Now we have already started talking about the atomic spectroscopy.

Remember we have already talked about the ICP-IES, so it is one kind of atomic spectroscopy. Now this ICP-IES is basically atomic emission spectroscopy, now we are going to talk about the atomic absorption spectroscopy, sometime it is generally denoted as AAS or double AS. Now this atomic absorption or double AA is based on the principle that a ground state atom is capable of absorbing light of the same characteristic wavelength as it would emit if excited to a higher energy level.

So, you can see here that a ground state atom is capable of absorbing light of the same characteristic wavelength as it would emit if excited to a higher energy level. So, every element for movement from this atom of every element, when it moves from ground state to the excited state, it basically absorb a characteristic wavelength of radiation. Now in flame atomic absorption, this is a type of atomic absorption we will discuss later.

Now in flame atomic absorption a cloud of ground state atom is formed by aspirating a solution of the sample into a flame so that is why it is called flame atomic absorption. So basically, a cloud of ground state atoms is formed by aspirating a solution of the sample into a flame of a temperature sufficient to convert the element to its atomic state. So this atomic absorption spectrometer basically allows the atoms from this ground state to absorb certain wavelengths of radiation to go to their excited state.

Now remember that the degree of absorption of characteristic radiation produced by a suitable source will be proportional to the population of ground state atoms in the flame and hence to the concentration of the elements in the analyte. So, more concentration of the elements in this ground state or more concentration of the atoms of a particular element in the ground state, it will absorb more characteristic radiation.

So, by this correlation we measure the concentration of a particular element through atomic absorption spectroscopy. You can see here there is an atomic absorption spectrometer and there are different types of attachment with it. We can attach the autosampler for automatic sampling, we can attach the hydride generation to enable it for measurement of arsenic and other elements specific metalloids. So this is a basic form of atomic absorption spectrometer.

(Refer Slide Time: 25:00)



Now let us move ahead and see the principle. So you can see that atomic absorption spectroscopy basically we are introducing a compound and we are basically giving it thermal energy by producing heat and then we are atomizing this compound. Now this heat we can give either through flame or through graphite furnace. Now when we basically produce the heat and produce the atoms it absorbs certain wavelengths of radiation and we can capture that.

The spectra of these atoms basically consist of the sharp lines as you can see here. This is all these sharp lines which are generated from the spectra of atoms. Now each element has a characteristic spectrum and due to sharpness of the lines there is a little overlap between the spectral lines. So the spectral lines are very narrow and sharp.

So as a result of that there is a very little overlap between the spectral lines of different elements, so therefore there is a very little interference. So that is why this instrument is more or less interference free.

(Refer Slide Time: 26:23)



Now we know that when we are introducing the sample and producing the high temperature by either through flame or through graphite furnace, we are producing vapors and we are basically measuring the absorbance or emission of the atomic wave. Now in case of AAS we are basically measuring the absorbance, we are not measuring the emission. For emission we are using the atomic emission spectroscopy. Now atomic spectroscopy deals with both absorbance and emission, however in case of AAS, we are specifically concerned about the absorption. So it deal with the atoms, so we cannot distinguish Fe2+ from Fe3+. So, this is basically the principle of atomic absorption spectroscopy.

(Refer Slide Time: 27:13)



Now regarding the sensitivity of the atomic absorption spectroscopy remember that atomic spectroscopy is very sensitive, it is a kind of atomic spectroscopy right. So this atomic spectroscopy is very sensitive for most of the elements and concentration at the ppm level may be routinely determined using flame atomization and we call it FAAS, flame atomic absorption spectroscopy or another way is using electrothermal atomization concentration at the ppb level.

So depending on the accuracy we want, depending on the level of detection we want, so if we are interested in the ppm level, then a flame atomic absorption spectroscopy is okay. However, if you want to go at the ppb level, then you have to go with the electrothermal atomization which is being given by graphite furnace. Now that is why this instrument is known as GFAAS or graphite furnace atomic absorption spectroscopy okay.

Now this is the principle of absorbance, you know all this. So absorbance is minus log by It by I0 where It is the transmitted radiation and I0 is incident radiation on the samples. So this is how this atomic absorption spectroscopy basically works.

(Refer Slide Time: 28:35)



So, this slide basically shows the schematic diagram of atomic absorption spectrometer. So basically, this is how it works. So basically first of all we introduce the sample in the nebulizer and we are injecting an oxidant which is generally air and then this sample with the oxidant moves to the cloud chamber and in the cloud chamber we introduce a fuel generally this is acetylene, sometime other gases are also used like hydrogen is also used.

So in the cloud chamber it will make a cloud of atoms and this cloud of atoms basically goes to the burner, and in the burner in the contact of the flame, so atoms will be in contact with the flame, and when they are contacting the flame they will absorb certain radiation. Now this characteristic radiation has to be produced from some source. So this source is basically this HCL or hollow cathode lamp.

And this hollow cathode lamp will produce a characteristic very narrow radiation or almost monochromatic radiation or wavelength which is basically being absorbed by this particular element which we are interested in and as a result of that after it absorb the radiation then we can get the transmitted radiation and then it moves to a monochromator to a detector and then amplifier and ultimately to the output.

So, from there we can get spectral lines and have an idea okay these are the wavelengths which they have absorbed and from there we can get the concentration of that particular element. Remember that this hollow cathode lamp is very specific to a specific element and this hollow cathode lamp generally utilizes a specific monochromatic radiation which is being absorbed by that particular element in which we are interested in.

So, this is how this AA spectrometer basically works. So, friends let us wrap up here and in the next lecture we are going to talk more about the hollow cathode lamp and then we will talk about other methods of inorganic pollutants and then we will be talking about the organic pollutant measurement method. Let us wrap up this. Thank you very much.