

Application of electrical resistivity tool to monitor soil contamination by herbicide

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The interpretation of the resistivity method depends on acquired resistivity contrast between the contaminated object and the host matrix. The present attempt reports preliminary understanding of the sensitivity of resistivity method to monitor herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) contamination in order to produce a reference dataset to develop a geophysical method to monitor soil bioremediation of herbicide-contaminated soil. Laboratory level experiments were carried out to define the correlation between herbicide concentration (H_c) and resistivity in non-polarizable (milli q double distilled water of 5.9 $\mu\text{s}/\text{cm}$ EC) and sandy soil matrix. The results confirm that the resistivity method can be used for the purpose of monitoring herbicide by adopting formation factor as 2.5 for the sandy soil matrix. The results indicate that moisture content of soil affects the resistivity parameter and it should be considered in the interpretation of data.

Keywords: Agriculture geophysics, contamination, electrical resistivity method, herbicide.

THE electrical resistivity method has emerged as a very effective tool in the characterization of contaminated regions and remediation monitoring studies^{1–4}. It is based on the hypothesis that resistivity changes take place due to the presence of inorganic/organic contaminants in the subsurface. It should be mentioned that resistivity is a bulk property and depends on various factors like density, moisture content, temperature, porosity, extent of moisture saturation, mineral content, etc.⁵. As contribution of these factors is significant on resistivity, determination of the effect of inorganic/organic contaminants on resistivity is complex; there will be a lot of uncertainty in the interpretation⁶. Hence, characterization of contaminants in the soil by resistivity technique requires more effort to

understand the alteration in resistivity occurring due to the inorganic/organic contaminants.

Resistivity technique is being used for detection and characterization of contaminants including organic, heavy metal, saltwater and leachate during the past few years^{4,7}. However, knowledge behind the link between contaminants and resistivity is still in its nascent stage and is an important area of research. In case of seawater, heavy metal, leachate and petrochemicals, there have been attempts to explore their electrical properties in the soil matrix and examine the sensitivity of geophysical tools to these contaminants. Though petrochemical contamination has been reported widely through geophysical methods^{8,9}, characterization of organic contamination in agriculture by geophysical tools has not been reported on the same scale. There is a pressing requirement to study the organic contamination in agriculture and associated resistivity signature. Significant efforts are required to develop the technique of resistivity signature as a tool for characterization of organic contaminants in agriculture.

Contamination of soil and water due to wide use of pesticides is of pressing concern to not only soil health, but also to the human health^{10,11}. Organic contaminants (pesticides) for their extensive use and persistent nature, can contaminate the soil and ground water for longer duration¹². Herbicides are group of pesticides which have highest application rate and are projected to have more use in future as well^{13,14}. Though herbicides are essential to control and eradicate weeds which rob nutrients and compete with crop plants, their excessive usage poses a potential risk to the environment^{15–17}.

The fate of herbicide in the environment is regulated by rainfall, microbial degradation and soil properties^{18,19}. Herbicides are directly applied on soil surface and some of it is likely washed out with rainwater/water leading to surface and groundwater contamination. The remaining herbicide may get adsorbed on clay and organic matter inducing its long time persistence in the soil^{20,21}. Herbicide can impede the biochemical process in the soil even before their degradation and ultimately also alter the soil properties. So, only a small fraction of chemical actually reaches the target organisms²² and impacts residual herbicides in soil and water. Hence, herbicide contamination leads to toxicological inference to the ecosystems and may lead to a negative impact on health of human, terrestrial and aquatic ecosystems^{23,24}.

Detection and monitoring of organic contaminants in agriculture (herbicide in this case) by resistivity technique has not been attempted so far. We have attempted here to understand the effect of herbicide on resistivity signature at laboratory level. We assess the effectiveness and sensitivity of resistivity technique to monitor the herbicide contamination in soil. We attempt to develop understanding for differentiating the contribution of herbicide and other factors in resistivity to establish its efficacy as an effective tool to monitor herbicides in the soil matrix.

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The present study is focused on (i) discussing the contribution of herbicide concentration, moisture content and density on the resistivity of the soil matrix; (ii) establishing the formation factor, and (iii) effect of herbicide concentration on electrical conductivity of water.

Towards the first objective, the experiment was carried out to assess the contribution of herbicide concentration, moisture content and bulk density of soil matrix on resistivity variation. 2,4-Dichlorophenoxyacetic acid (2,4-D) was chosen due to its extensive usage and being one of the oldest herbicides which has been one of the important constituents of agent orange²⁵. In all the experiments, agriculture grade 2,4-D (ADMA India Pvt. Ltd.) was used with 59% 2,4-D, 30% sequestering agent dimethyl amine, 1% lignin sulphonate and 10% diluent. Resistivity measurement was carried out using columns with dimensions of 12 cm height and 2 cm radius. Soil sample used had sandy loam texture. The soil was sieved and oven-dried overnight (at 105°C) to make it a homogenized medium. Four-electrode method was adopted for resistivity measurement. After each measurement, the column was weighed and oven-dried overnight at 105°C to obtain the bulk density and moisture content of the sample. For the next measurement, new homogenized soil sample was

taken and the above process was repeated at different concentrations of herbicide.

It was observed (Figure 1) that as herbicide concentration increases, the bulk resistivity decreases. The regression analysis of resistivity and herbicide concentration shows that 87% of the variability in resistivity is explained by regression of herbicide concentration on resistivity which indicates that the resistivity is linearly correlated with herbicide concentration. The results (Table 1) show higher correlation between the resistivity and herbicide concentration (-0.8) than resistivity and moisture content (-0.6) and resistivity and density (-0.3). The effect of moisture content is significant, considering that the correlation with resistivity is -0.6 as compared to the herbicide concentration. It is important to consider the moisture concentration while, associating the bulk resistivity property to any contaminants. Hence, a laboratory experiment was carried out in saturated condition wherein, the resistivity signatures of the interaction of herbicide–water mixtures are evaluated.

Towards the second objective, resistivity measurement in saturated condition was carried out by adopting the Tracer Test Method²⁶. The experimental arrangement is shown Figure 2. Soil column of 10 cm diameter and 22 cm height was fully saturated by milli q double distilled water (5.9 $\mu\text{s}/\text{cm}$ EC). Later, herbicide (0.8 ohm-m) was introduced by continuous flow system. The apparent resistivity at 5 levels ($\rho_1, \rho_2, \rho_3, \rho_4, \rho_5$) was recorded at hourly intervals (Figure 3) using Wenner arrangement.

Breakthrough curves of all the levels $\rho_1, \rho_2, \rho_3, \rho_4, \rho_5$ show decrease in resistivity as time progresses, which indicates that the contribution of herbicide in resistivity variation is prominent. The resistivity varies from moderate 40 ohm-m to highly conductive 1 ohm-m. Different breakthrough start and endpoints were observed (Table 2). The breakthrough starts very early in ρ_4 and ρ_5

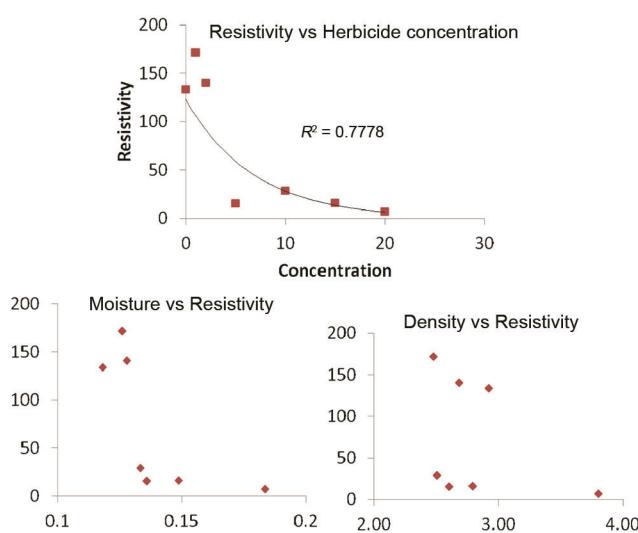


Figure 1. Resistivity data as recorded during the experiment.

Table 1. Correlation matrix among herbicide concentration, resistivity, bulk density and moisture content

	Herbicide concentration	Resistivity	Density	Moisture
Herbicide concentration	1			
Resistivity	-0.81	1		
Density	0.66	-0.37	1	
Moisture	0.92	-0.68	0.83	1

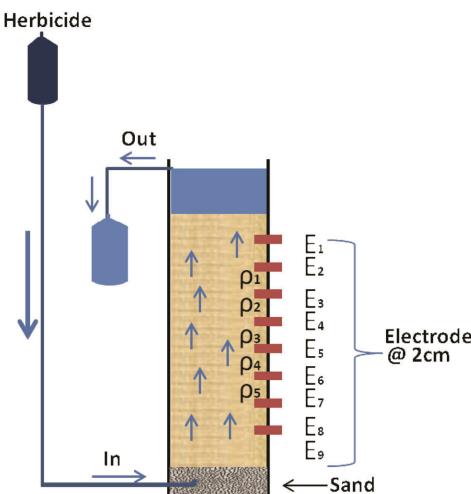


Figure 2. Experimental arrangement for controlled column experiment.

(30 min) as it was closer to source and in ρ_1, ρ_2, ρ_3 at 9, 5, 3 h respectively. In all levels $\rho_1, \rho_2, \rho_3, \rho_4, \rho_5$, breakthrough ends at nearly 10 h time duration. At the end edges of the graph, it is believed that the soil bed is fully saturated by the herbicide. For the interpretation of resistivity data, Archie's Law¹³ is commonly adopted. Hence, the resistivity value of fully saturated soil by brine herbicide and bulk resistivity of the matrix can be related by using Archie's Law (eq. (1))

$$\rho_s = F \frac{\rho_w}{S_w^n}, \quad (1)$$

where ρ_s is the resistivity of saturated formation, ρ_w the brine resistivity, S_w the brine saturation and F is the formation factor.

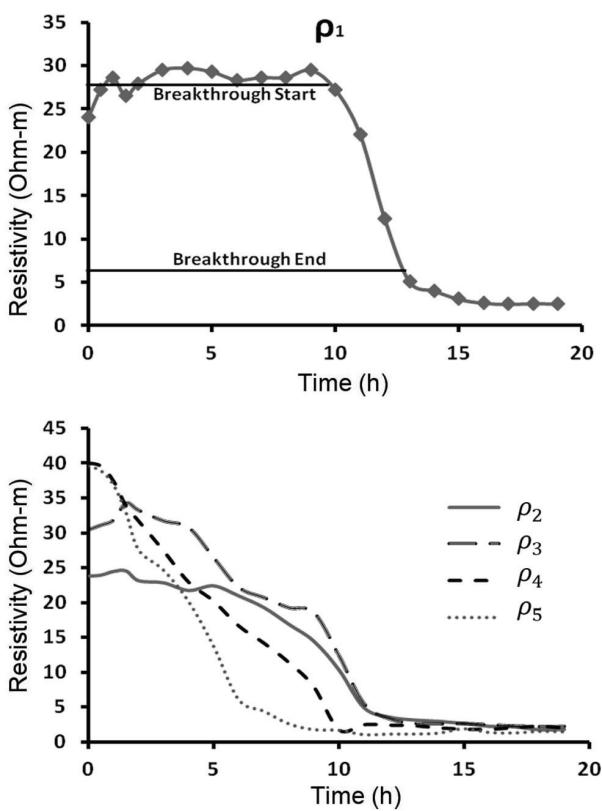


Figure 3. Breakthrough curve for $\rho_1, \rho_2, \rho_3, \rho_4, \rho_5$ as obtained from tracer test method.

Table 2. Breakthrough start and end time and formation factor

	Breakthrough start (h)	Breakthrough end (h)	Formation factor
ρ_1	9	13	3.6
ρ_2	5	12	2.2
ρ_3	3	11	2.7
ρ_4	½	10	2.4
ρ_5	½	8	1.7

Formation factor was calculated by the following equation

$$F = \frac{\rho_s}{\rho_H}, \quad (2)$$

where ρ_H is the resistivity of herbicide.

From eq. (2), the formation factor of experimental soil for herbicide was calculated for all the resistivity levels (Table 2). The difference in the estimated formation factor is an effect of different packing density and non-homogeneous soil content and uneven pore distribution. The average formation factor recorded was 2.5. The determination of formation factor will facilitate the determination of the brine concentration.

The electrical conductivity of the herbicide mixed with water solution with different concentrations was measured in the laboratory with Tabletop EC meter. Samples were prepared by adding different concentrations of herbicide in milli q double distilled water ($5.9 \mu\text{s}/\text{cm}$ EC). After shaking for 24 h at 70 rpm, EC of the mixed solution was measured.

Figure 4 shows the relationship between EC of water and herbicide concentration. The figure shows that, herbicide up to 40% concentration increases the electrical conductivity of water in a linear manner. When the herbicide concentration in water exceeds 40%, EC starts declining. The regression analysis reflected that 95% of variability in resistivity can be explained by regression of herbicide concentration on resistivity. The relationship between resistivity and herbicide concentration is expressed as

$$H_c = 0.12 \left(\frac{1}{\rho} \right)^3 - 27.9 \left(\frac{1}{\rho} \right)^2 + 1705.4 \left(\frac{1}{\rho} \right) + 3080.3. \quad (3)$$

Based on the above experiments, it can be established that the resistivity parameter is sensitive to the presence of herbicides in the soil matrix and therefore, it can be used for characterization of the soil contaminated by herbicides. The behaviour of breakthrough curves at different levels indicates the migration of herbicide within the

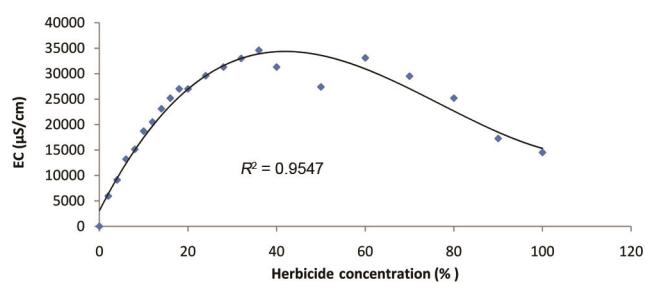


Figure 4. Relationship between herbicide concentration in water and EC.

soil column, which proves the ability of the resistivity to monitor the herbicide in the soil. As herbicide is very conductive in nature and its interaction with water causes hydrolysis producing more ions, certain precautions, such as monitoring the water content in the soil matrix should be carried out. Interpretation of resistivity method depends on the resistivity contrast between the anomalous body and the host matrix. At present, the application of resistivity tool has so far been restricted to certain cases, viz. highly contaminated sites such as saline water, spillage from petroleum storage and landfills. There is a strong need for improvement in methods and instruments to monitor small scale chemical contamination which is an emerging threat to environment and human health. Further, this method needs to be developed to assess its sensitivity to monitor soil bioremediation of herbicide contamination which would be a significant contribution of geophysicists towards protection of environment from persistent organic pollutants.

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