# Identification of Flowpaths Using Chemical Fingerprint of Soilwater

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## 1. Introduction

The movement of contaminants in groundwater and in the unsaturated zone is a problem often encountered in the practice of Environmental and Hydraulic Engineering. The possibility of using spatial and temporal variations of ions to identify the subsurface flow paths was investigated in a series of field and laboratory experiments. The chemical analysis show that rainwater and streamwater have different characteristics. The change in chemistry occurs during the passage of water through the soil. This chemical behavior can be used to identify the path taken by the soil water. This study was different from previous studies as it attempted to look into the chemistry of soil water, during rainfall events, thereby trying to ascertain the changes that occur in the soil water.

The study site was a weathered granitic hillslope near Kanedaira dam in Gifu Prefecture. This catchment has a top soil layer of about 1 m, and is underlain by weathered granite. The mean slope is about 30°. A complete description of the study site is given in Matsubayashi et al. (1990). The streamwater in this catchment has shown Ca<sup>++</sup> peaks with flood hydrograph peaks and drops in Na<sup>+</sup> at the same time. In trying to explain this phenomena, laboratory experiments on a granite core using chemical inputs (NaCl and CaCl<sub>2</sub>) has shown preferential absorption of Na and release of Ca from the weathered granite layer underlying the top soil layer (Matsubayashi et al., 1995).

## 2. Sampling procedure and analysis

Soil water samples were obtained using ceramic samplers. Samples were obtained hourly during rainfall events at 3 levels (7, 25 and 50 m from the stream) in the experimental hillslope, at four depths (10, 30, 60 and 100 cm) at each level. Rainfall and streamflow data, variation of soil water potentials with depth during the rain events, Specific conductivity and pH values of rain, soilwater and streamwater were also obtained. Ionic concentrations Na<sup>+</sup>, NH4<sup>+</sup>, K<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, F<sup>-</sup>, Cl<sup>-</sup>, NO3<sup>-</sup> and SO4<sup>--</sup> were analyzed using liquid chromatography and HCO3<sup>-</sup> was analyzed by titration. Since the chemical behavior of all these ions is a broad topic, the behavior of the cation Ca<sup>++</sup> and anion SO4<sup>--</sup> and their implications on flowpath identification is discussed in this short paper.

## 3. Results and Discussion

The spatial and temporal variation of the selected ions (Ca<sup>++</sup>, and SO4<sup>--</sup>) and the data for two rainfall events are shown in Figures 1 and 2, as a typical result. The two rainfall events were selected on the basis of the antecedent rainfall (162 mm in preceding 10 days for July 5th and 31 mm in preceding 10 days for September 16th). The time shown in the time axis is the sampling time, therefore the concentrations shown are for the one hour averaged sample.

Both Ca<sup>++</sup> and SO<sub>4</sub><sup>--</sup> are dominant in top soil layers. The main source of sulfate ion is atmospheric input. Calcium is generally controlled by atmospheric input and by the dissolution of the silicate minerals and reactions in the carbonate system. In the present study we could analyze the chemical input to the soil as well as the chemical variation in the overlying topsoil layer during rainfall events. Analysis of rainwater showed that the contribution from rainfall loading of Ca<sup>++</sup> is low (0.01 meq/L). The rainfall input of sulfate ion also was on average 0.02 meq/L, a low value compared with soilwater and streamwater concentrations.

The tensiometer data indicates that when there is not much antecedent rains (e.g. September 16th rainfall event), the surface soil in the top 30 cm layer will get almost saturated during the rain peak, whereas the 60 cm layer will respond only slightly and no response at all from the 100 cm layer. For the rain of July 5th, the tensiometer data showed near saturation of the bottom granite layer at 100 cm.

Looking at the SO4<sup>--</sup> ion behavior in the soil, we can see that on 7/5 there is a clear demarcation of SO4<sup>--</sup> concentration i.e., the ion concentrations in different soil layers changed only in a small range, throughout the rain event. Whereas on 9/16 it shows a wider fluctuation of concentration, with 60 and 100 cm layers showing high concentrations 2 and 3 hours after the start of the rain event.

The Ca<sup>++</sup> ion also shows similar type of behavior for the two rainfall events. Looking at these ion data we can argue that the rain input flowed laterally on 7/5 and there was vertical infiltration on 9/16th.

This behavior shows that when the top surface was dry (Low antecedent rain), the moving water carried the surface dominant ions to the bottom layer. When the bottom layers were saturated, the behavior shows lateral flows, as the ion concentrations are not intermixed in different layers. Looking at the rainfall data, and considering antecedent rainfall and tensiometer data, we can say that the rainfall water has infiltrated almost vertically in to the soil on 9/16 th, whereas the water flowed laterally on 7/5th, supporting the verdict given by the ion behavior.

When we look at two dominant ions in the surface soil, SO4-- and Ca<sup>++</sup> the question arises why the Ca shows some concentration fluctuation even on July 5th at 30cm and 60 cm while SO4-- shows a good separation. The answer to this may be due to cation exchange, even in the top soil layer. Further work (laboratory experiments) are being carried out to support this initial assumption.

### 4. Conclusion

The ion concentration variation with depth and their lag times confirm near vertical movement of water during rain events for low antecedent rainfall and lateral movement when the soil is nearly saturated, further supported by the tensiometer data. The rainfall intensity may also have an effect on this flowpath. The results of the field investigations suggest the effect of cation exchange process, at different soil layers.

#### 5. References

Matsubayashi et al. (1990), Journal of HydroScience. & Hydraulic Engineering., 7:2:225-232 Matsubayashi et al. (1995), Proceedings of the 50th Annual Conference, JSCE, 2-(A), 154-155

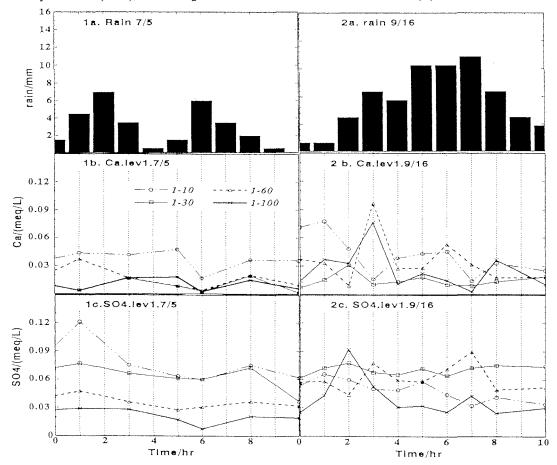


Fig 1. Rain, Ca<sup>++</sup> &SO<sub>4</sub><sup>--</sup> data, July 5

Fig 2. Rain, Ca++ &SO4-- data, Sept 16