# Comments on 'Empirical modelling of the kinetics of phosphate sorption to macropore materials in aggregated subsoils' by H.C.B. Hansen, P.E. Hansen & J. Magid

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# Letters to the Editor

## Comments on 'Empirical modelling of the kinetics of phosphate sorption to macropore materials in aggregated subsoils' by H. C. B. Hansen, P. E. Hansen & J. Magid

Sorption of phosphorus (P) on to soils is important both for agronomic and for environmental reasons. Sorption kinetics, studied in the laboratory, tells us what we could expect with respect to the long-term behaviour of P in the field.

Hansen *et al.* (1999) studied the kinetics of P sorption on to four soil materials, and developed a new (empirical) model for describing their results. They reject other commonly used models, and propose the use of a model that predicts (i) a short phase with very fast sorption, (ii) a 'lag phase' in which no sorption occurs, followed by (iii) a phase in which P in solution decreases with time (linearly on a double logarithmic scale). As explained below, I have doubts on (1) the method used by the authors, and do not agree with (2) their criticism and (3) the proposed alternative. Also, an additional remark is made on (4) the fitting procedure for the Langmuir equation.

### 1 *Method used for studying sorption kinetics*

The four soils studied had a pH (in water) of 7.16, 6.48, 5.59 and 6.34, respectively. Before P was added, the soils were pre-equilibrated for 24 h at pH 5.0 by adding HCl. One may expect that the soils had reached a certain P sorption equilibrium at their original pH when present in the field. Lowering the pH would disturb this equilibrium: in general, the capacity of (hydr)oxides to sorb P strongly increases with a decrease in pH. The medium used to study sorption was 0.01 M $CaCl_2$, at a solution:soil ratio of 100 ml:1 g soil, which is fairly large. It is known that adding Ca to a soil can lead to stronger binding of P (Ryden & Syers, 1975). Both conditions (low pH and much Ca) will disturb the soil's equilibrium with P, and will probably lead to a fast sorption when the soil is brought into contact with P. This must be seen as an experimental artefact, and not as a part of the soil's 'normal' kinetic sorption behaviour. The amount of P sorbed fast will be (slowly) redistributed over sorption sites within soil aggregates, without directly diminishing the external P concentration, which is measured as a 'lag phase'. An indication that the decrease in pH played a role in the lag phase is the fact that the Albic soil studied did not show this phase. This soil had a pH ($H_2O$) of 5.59, by far the closest to 5.0 at which sorption was studied.

### 2 *Criticism of existing models*

The main reason why, for example, the modified (kinetic) Freundlich equation,

$$Q = a\, t^m\, C^n \qquad (1)$$

(Kuo & Lotse, 1973; Barrow & Shaw, 1975), is not used by the authors is because the Freundlich isotherm predicts a continuous sorption, without reaching a maximum. However, the alternative used by the authors for describing the slow sorption phase, $P_{\mathrm{sol}} = K\, t^{-B}$, also does not predict that $P_{\mathrm{sol}}$, the concentration in the solution, becomes constant due to reaching of a sorption maximum. The attractiveness of the kinetic Freundlich equation is that, for a large number of soils, it has proved to be able to describe P sorption, with three parameters, over a wide range of initial concentrations during a long period (weeks or months; see for example References cited in Chardon & Blaauw, 1998). Re-examination of the data of Hansen *et al.* (1999) by Barrow *et al.* (2000) indeed showed that an extended version of Equation (1) can adequately describe the data.

### 3 *Proposed alternative method*

The alternative used by Hansen *et al.* requires for each initial concentration (i) determination of the fast amount sorbed, (ii) the period of this phase, and (iii) parameters of the equation describing the slow phase. No indications are given by the authors on how the change in total sorption with time can be described for a given soil, over a range of P additions.

### 4 *Fitting procedure for the Langmuir equation*

The authors suggest using a logarithmic form of the Langmuir sorption equation for fitting purposes, and not a linearized form. It is well known that linearization of the equation can lead to severe errors in estimated parameters (Harter, 1984), so presenting an alternative is recommended. Since a logarithmic fit is common only with the Freundlich equation, to my knowledge, details of the proposed fitting procedure should be given. However, Figure 1 in Hansen *et al.* (1999) shows that the calculated curves for two soils (Red and Btg, both 7 days' sorption) lead to an incorrect (too small) sorption maximum.

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## A comment on 'Efficacy of perforating the soil to capture and store rain during fallow in dry regions' by S. R. Cattle

In his paper, S. R. Cattle (1999) reports an alternative to tillage, tillage which, if repeated regularly, leads to soil structure degradation. It consists of perforating the soil with artificial macropores that are expected to increase infiltration of water. Then, the question addressed by the author is: does the effect of perforating the soil benefit water storage considering that this practice may also increase evaporation?

The first part of the experiments deals with the influence of such artificial macropores on water infiltration and runoff. However, attention focuses on the analysis of the influence of the macropores on time-to-ponding, which is somewhat surprising. It is clear that an increase in time-to-ponding is generally associated with an increase in infiltration, but I think it is no longer the case when the increase in infiltration is obtained by modifying only locally the infiltration characteristics of the soil. The physical definition of time-to-ponding is the time at which soil surface water content reaches saturation and water begins to accumulate or flow on the soil surface. In the experiment described by the author, the area of cross-section of the macropores in the horizontal plane is about 0.7% of the plot area. The soil properties are unchanged on the other 99.3% of the surface, and there is no reason that the time-to-ponding should increase. The time-to-ponding is sometimes also defined as the time at which runoff begins at the outlet of a small experimental plot. Even with this definition, it is unlikely that runoff will be totally intercepted by macropores before reaching the outlet of the plot. We should thus expect time-to-ponding to be unaffected by macropores, and this is actually what I conclude from the author's experimental results, contrary to what he writes on this point. It is only because he used the definition of time-to-ponding proposed by Bridge & Ross (1985), which is the time at which half the area of the plot consisted of puddles, that the author could expect an effect of macropores on time-to-ponding.

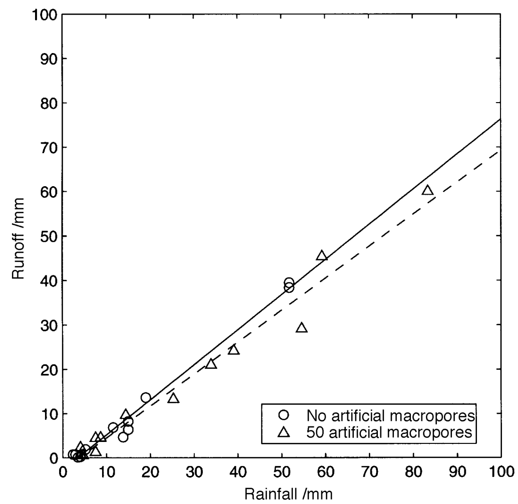


**Figure 1** Influence of artificial macropores on runoff volume measured after a rain event.

More important than the discussion about what definition of time-to-ponding to use is the fact that the data presented by the author do not allow an estimate of the quantity of water entering the soil resulting from the presence of macropores during an entire rainfall event. This is the information required to evaluate the author's proposition and his experiments should have permitted such results to be obtained. I have done such an estimation from an experiment I conducted in Niger. The study site was in a fallow, bare, crusted soil. Runoff volume was measured from a 1 square metre plot after each rain event of the 1997 rainy season. During the first part of the season, no special treatment was applied to the plot. At mid-season, the soil was perforated with 50 artificial macropores, more or less uniformly distributed, with a mean diameter of 9 mm and a mean depth of 270 mm. The artificial macropores therefore covered 0.3% of the plot area. Figure 1 shows runoff volumes, $R$, against rainfall volumes, $P$, for the entire season, and the two associated relations obtained by fitting to the data the following model:

$$R(P) = \kappa(P - \phi), \tag{1}$$

where $\kappa$ is $\mathrm{d}R/\mathrm{d}P$ and $\phi$ is the value of $P$ for which runoff begins. It is clear that macropores have no effect on the parameter $\phi$ ($\phi_1 = 3.2$ mm, $\phi_2 = 3.1$ mm), and thus, despite the presence of macropores, runoff appears even for a rain event of a few millimetres. The presence of the macropores has a small effect, but significant at the 10% error rate, on the slope of $R(P)$: $\kappa_1 = 0.91$, $\kappa_2 = 0.83$, which means that a certain proportion of runoff is captured by the macropores. In this case coring has an effect of 9–10%.

Let us consider the case of $N$ macropores of diameter $d$ randomly distributed on a ponded inclined plane of downslope length $L$ and width $l$, at steady state under a rainfall intensity $r$. The flow rate per unit width at a distance $x$ from the top of the inclined plane is $rx$. We assume that all the water intercepted by a macropore infiltrates. From experimental observations (Léonard *et al*., 1999), in the case of an inclined plane, we can estimate the water flux entering a macropore as the product of the flow rate per unit width at the macropore location and the macropore diameter. The water flux to a single macropore is thus $rxd$, and because the macropores are randomly distributed between $x = 0$ and $x = 1$, the average water flux to a single macropore is $0.5rLd$, and the water flux entering all the macropores is $0.5NrLd$. The ratio of macropore flow to total flow is $0.5NrLd/rLl$ or $0.5Nd/l$. With $N = 50$, $d = 9$ mm and $l = 100$ cm the ratio obtained is 22.5%, which is above our experimental value of 9–10%, despite the fact that an inclined plane does not favour an excessive effect of macropores because of the absence of depressions that drain large microcatchments. There may be four main reasons for the observed effect to be less than expected, as follows.

**1** As stated by Cattle, it is possible, although quite improbable with $N = 50$, that most of the macropores are in areas with little coalescing water.

**2** By assuming that all the water intercepted by a macropore infiltrates, we neglect the finite infiltration capacity of macropores which might result in macropores filling with water. However, in our case, the infiltration capacity of macropores is governed by the infiltration capacity of the soil sandy matrix which is very large.

**3** It was observed that a sufficient water depth is sometimes necessary to initiate flow in a macropore. It is likely that such a water depth was not reached for all macropores and that water did not enter some of them.

**4** During the second part of the season, overall because of the occurrence of an exceptional rainfall event (80 mm), the macropores partly filled with sediments, their potential effect being thus reduced.

Despite the fact that our 50 artificial macropores increase infiltration by only 10%, if we consider, from the results of Cattle, that the difference in the evaporation rate between perforated and non-perforated soil is of the order 0.1–0.2 mm day$^{-1}$, we can think that perforating the soil with artificial macropores benefits water storage. In addition (Léonard & Rajot, 1997), macropores made by termites appear to be more effective and durable than artificial ones, which deteriorate quickly, leading to enhanced infiltration.

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## Reply to comment on 'Efficacy of perforating the soil to capture and store rain during fallow in dry regions' by J. Léonard

Dr Léonard offers some relevant comments on the efficiency of individual macropores in harvesting ponded rainfall, and presents some data to show that populations of artificial macropores do not necessarily harvest water as well as we might expect. I concur with the notion that artificial macropore regimes, as described in Cattle (1999), are unlikely to intercept all ponded water during moderate or heavy rain. However, I reiterate that individual artificial macropores may serve to prolong the time-to-ponding (and therefore increase infiltration) at a local scale if they are positioned within a depression of a microcatchment. The extent to which an individual macropore prolongs local surface ponding will depend on factors such as the interception and connectivity of pre-existing subsoil porosity, the stability to wetting of this soil, and the rapidity of macropore infilling by sediment and debris. Clearly, each artificial macropore has only a finite capacity to harvest water, and so we cannot expect that a regime of such macropores will capture as much water as predicted by Dr Léonard's model of water flow over an inclined plane, as this model assumes a constant flow of water into each artificial macropore. The efficacy of a particular perforation regime under a rainfall event will be reflected by how similar are the modelled and actual water capture by artificial macropores.

I cannot fully comment on the Niger data collected by Dr Léonard, as critical auxiliary data such as the topsoil's antecedent water content at each rainfall event and the rainfall event intensities are not provided. As indicated in other papers, such as Bowyer-Bower (1993), more intense rain on to initially moist topsoil will provide a greater opportunity for runoff, and consequently for macropores to harvest the ponded water. Without an indication of these properties, it is difficult to determine whether the different runoff rates for the perforated and unperforated treatments in Niger reflect inefficient harvesting of water by the artificial macropores or an overwhelming effect of very intense rain. I would be interested to compare Dr Léonard's full data set with that documented in Cattle (1999), as I believe this is a promising water harvesting strategy in semi-arid areas.

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