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Environnement Canada

Geochemical Stability of Phosphorus Solids
below Septic System Infiltration Beds

By:

M. Zurawsky, W. Robertson, C. Ptacek, S. Schiff

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Abstract

In a recent review of 10 mature septic system plumes, it was recognized that precipitation of phosphorus (P) commonly occurred in close proximity to the infiltration pipes, resulting in discrete narrow intervals enriched in P by a factor of 2-4 (Robertson et al., 1998; Zanini et al., 1998). Although these attenuation reactions appeared to be sustainable, questions have arisen regarding the potential for remobilization of this P mass, should geochemical conditions change. To test the stability of these P solids, dynamic flow column tests were carried out using sediments from three of the previously studied sites (Cambridge, Langton and Muskoka). Tests focused on sediments from two intervals, the 'High P' zones and the underlying sediments with lower total P content ('Below' zones). The columns were eluted with DI water, or calcite-saturated DI water, at loading rates leading to hydraulic retention times of 1-2 days. Tests were continued for 160-270 pore volumes, during which time varying degrees of saturation were maintained in the columns. During saturated flow conditions, relatively high concentrations of PO_4 were eluted from Cambridge and Langton high P zones (up to 4 and 9 mg L^{-1}, respectively), accompanied by elevated concentrations of Fe (up to 1.4 mg L^{-1}) and Mn (up to 4 mg L^{-1}) and lower values of Eh (< 150 mV). The 'Below' zones at Cambridge and Langton however, maintained lower concentrations of P (generally < 2 mg L^{-1}), Fe (<0.2 mg L^{-1}) and Mn (< 1 mg L^{-1}) and maintained higher Eh (> 250 mV) during saturated flow conditions. During unsaturated flow, P and Fe declined dramatically in the high P zones (P < 1 mg L^{-1}, Fe < 0.2 mg L^{-1}), whereas concentrations remained about the same as during saturated flow in the 'Below' zones. This behaviour is attributed to the development of reducing conditions during saturated flow in the high P zones, leading to the reductive dissolution of Fe(III)-P solids present in the sediments. Reducing conditions did not develop in the 'Below" zones apparently because of lower organic carbon contents (0.03-0.04 wt %) compared to the high P zones (0.2-0.65 wt %). At the Muskoka site, where the sediments were noncalcareous, low values of P (< 0.2 mg L^{-1}) were maintained throughout. Results indicate the possibility of remobilizing P minerals precipitated below septic system infiltration beds should more reducing conditions develop. This could occur if sewage loading patterns change, for example when a lakeshore seasonal cottage is converted to a permanent dwelling.

Stabilité géochimique de matières solides riches en phosphore sous les lits d'infiltration des fosses septiques

M. A. Zurawsky, W. D. Robertson, C. J. Ptacek et S. L. Schiff

Résumé

Lors d'un examen récent de dix panaches matures de fosses septiques, on a remarqué qu'il y avait souvent des précipitations de phosphore (P) dans le voisinage immédiat des tuyaux d'infiltration, ce qui créait d'étroites bandes de sol enrichi en P par un facteur de 2 à 4 (Robertson *et al.*, 1998; Zanini *et al.*, 1998). Même si ces réductions semblaient durables, on s'est demandé si cette masse de P pouvait être remobilisée si les conditions géochimiques changeaient. Afin de vérifier la stabilité de ces matières solides riches en P, on a effectué des essais d'écoulement dynamique sur colonne en utilisant des sédiments de trois sites déjà étudiés (à Cambridge, Langton et Muskoka). Ces essais portaient surtout sur des sédiments de deux types de zones, ceux à forte teneur en P et sur les sédiments sous-jacents à plus faibles teneurs totales en P (zones sous-jacentes). La contenu de la colonne était élué avec de l'eau désioniseé, ou avec de l'eau désionisée saturée en calcite, à des taux de charge correspondant à des temps de rétention hydraulique de 1 à 2 jours. On poursuivait ces essais jusqu'à l'obtention d'un volume égal à 160-270 fois celui des eaux de porosité, pendant qu'on maintenait divers taux de saturation dans la colonne. Dans des conditions d'écoulement à saturation, des concentrations relativement élevées de PO_4 étaient éluées d'échantillons de zones à forte teneur en P de Cambridge et de Langton (pouvant atteindre 4 et 9 mg L^{-1}, respectivement), avec de fortes concentrations de Fe (pouvant atteindre 1,4 mg L^{-1}) et de Mn (pouvant atteindre 4 mg L^{-1}) et des faibles valeurs d'Eh (< 150 mV). Toutefois, on observait des concentrations inférieures de P pour les zones sous-jacentes de Cambridge et de Langton (habituellement < 2mg L^{-1}), ainsi que de Fe (<0,2 mg L^{-1}) et de Mn (< 1mg L^{-1}), avec de plus fortes valeurs d'Eh (> 250 mV) dans des conditions d'écoulement à saturation. Lors de l'écoulement dans des conditions d'insaturation, on observait une forte diminution des concentrations de P et de Fe dans les zones à fortes teneurs en P (P < 1 mg L^{-1}, Fe < 0.2 mg L^{-1}), alors que concentrations restaient à peu près les mêmes que celles notées pendant les écoulements à saturation pour les zones sous-jacentes. On attribue ce comportement au développement de conditions réductrices pendant l'écoulement à saturation dans les zones à forte teneur en P, ce qui entraînait la dissolution dans des conditions réductrices des matières solides riches en Fe(III) et en P présentes dans les sédiments. Ces conditions réductrices ne sont pas apparues dans les zones sous-jacentes, apparemment à cause de plus faibles teneurs en carbone organique (0,03 à 0,04 % en poids) par rapport à celles des zones à fortes teneurs en P (0,2-0,65 % en poids). Au site de Muskoka, dont les sédiments étaient non calcaires, on observait de faibles valeurs de P (< 0,2 mg L^{-1}) pendant toute la période des mesures. Ces résultats indiquent la possibilité de remobilisation des minerais phosphatés précipités sous les lits d'infiltration des fosses septiques si des conditions réductrices apparaissent en cas de changement des conditions des charges d'eaux usées, par exemple si un chalet saisonnier au bord d'un lac est converti en résidence permanente.

NWRI RESEARCH SUMMARY

Plain language title
Long-term Leaching of Phosphorus from Aquifer Solids

What is the problem and what do sicentists already know about it?
The release of phosphorus to surface waters results in the stimulation of nuisance algae and the general degradation of water quality. Untreated wastewater contains elevated concentrations of nutrients, including phosphorus. Removal of phophorus at wastewater treatment plants prior to discharge helps to minimize the occurrence of eutrophication. In many areas of Canada, wastewater is discharged to the subsurface through tile-bed leaching fields. These leaching fields result in the partial removal of phosphorus, however, a portion of phosphorus is transmitted through the groundwater zone and is discharged to surface waters. The extent to which the phosphorus is removed is dependent on local soil and geological conditions, wastewater loading rates and groundwater flow rates. Previous studies suggest that phosphorus removal can range from near complete removal to minimal removal. Septic systems, therefore, represent a potentially significant source of phosphorus in many watersheds and a major cause of eutrophication of small lakes and rivers.

Why did NWRI do this study?
This study was initiated to evaluate geochemical mechanisms controlling the natural removal of phoshorus and to determine the longevity of these reactions. Understanding the natural removal processes is an important step in determining the phosphorus release rates and to develop plans for the sustainable development of lakeshore properties. Cores of aquifer solids were collected within tile beds at several locations in Ontario and the aquifer materials were leached under various geochemical conditions to assess the potential for long-term attenuation of the phosphorus.

What were the results?
The results indicate that there is initial attenuation of phosphorus below tile-bed leaching lines, but that this phosphorus can be readily leached under mildly reducing conditions. The results suggest that there is the potential for phosphorus leaching at unacceptable concentrations for many years after tile bed abandonment. The leaching is particularly extensive in aquifer materials that are naturally reducing.

How will these results be used?
The results will be used by engineers and environmental scientists responsible for wastewater disposal and land-use planning in areas with sensitive lakes. Many lakes in Canada and elsewhere in the world are becoming increasingly eutrophic as a result of phosphorus leaching from septic systems. The results are particularly important in rural, semi-rural and resort settings where septic systems are widely used.

Who were our main partners in the study?
University of Waterloo, CRESTech

Sommaire des recherches de l'INRE

Titre en langage clair
Lixiviation à long terme du phosphore des matières solides des aquifers

Quel est le problème et que savent les chercheurs à ce sujet?
Le rejet de phosphore dans les eaux de surface stimule la croissance des algues nuisibles et favorise la dégradation générale de la qualité de l'eau. Les eaux usées non traitées contiennent des fortes concentrations de nutriments, notamment de phosphore. L'élimination de ce phosphore par les stations d'épuration des eaux usées permet de réduire au minimum l'eutrophisation. Dans beaucoup de régions du Canada, on rejette les eaux usées dans le sol par l'intermédiaire de champs de percolation à lit dallé. Ces champs assurent l'élimination partielle du phosphore, mais une portion de ce dernier traverse la zone des eaux souterraines et atteint les eaux de surface. Le degré d'élimination du phosphore dépend du sol et des conditions géologiques locales, des taux de charge des eaux usées et des débits d'écoulement des eaux souterraines. Les études antérieures semblent indiquer que l'élimination du phosphore peut varier fortement, de quasi complète à très faible. Donc, les fosses septiques constituent une source de phosphore qui peut être importante dans beaucoup de bassins hydrographiques, et une cause majeure d'eutrophisation des petits lacs et cours d'eau.

Pourquoi l'INRE a-t-il effectué cette étude?
On a entrepris cette étude pour évaluer les mécanismes géochimiques régissant l'élimination naturelle du phosphore et pour déterminer la longévité de ces réactions. La compréhension des processus naturels d'élimination est une étape importante pour la détermination des vitesses de libération du phosphore et pour l'élaboration de plans de développement durable des propriétés riveraines. On a prélevé des carottes de matières solides des aquifères dans des lits dallés à plusieurs endroits en l'Ontario, et on a soumis ces matières à un traitement de lixiviation dans diverses conditions géochimiques afin d'évaluer la réduction à long terme des concentrations de phosphore.

Quels sont les résultats?
Les résultats indiquent qu'il y a eu une réduction initiale du phosphore sous les tuyaux de lixiviation des lits dallés, mais que ce phosphore peut être facilement remobilisé dans des conditions faiblement réductrices. Il semble donc possible que le phosphore soit lixivié à des concentrations inacceptables bien des années après la désaffectation d'un lit dallé. Cette lixiviation est considérablement plus forte dans les aquifères formés dans des matières naturellement réductrices.

Comment ces résultats seront-ils utilisés?
Ces résultats serviront aux ingénieurs et aux spécialistes de l'environnement responsables de l'élimination des eaux usées et de la planification de l'aménagement du territoire dans les régions à lacs vulnérables. Beaucoup de lacs du Canada et d'autres pays deviennent de plus en plus eutrophes à cause de la lixiviation du phosphore des fosses septiques. Ces résultats sont importants notamment pour les régions rurales, semi-rurales et pour les lieux de villégiature, où les fosses septiques abondent.

Quels étaient nos principaux partenaires dans cette étude?
Université de Waterloo, CRESTech

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March 17, 2002

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In a recent review of 10 mature septic system plumes, it was discovered that precipitation of phosphorus (P) commonly occurred in close proximity to the infiltration pipes, resulting in discrete narrow intervals enriched in P by a factor of 2-4 (Robertson et al. 1998; Zanini et al. 1998). Although these attenuation reactions appeared to be sustainable, questions have arisen regarding the potential for remobilization of this P mass, should geochemical conditions change.

To test the stability of these P solids, dynamic flow column tests were carried out using sediments from three of the previously studied sites (Cambridge, Langton and Muskoka). Tests focused on sediments from two intervals; the 'High P' zones and the underlying sediments with lower total P content ('Below' zones). The columns were eluted with DI water, or calcite-saturated DI water, at loading rates leading to hydraulic retention times of 1-2 days. Tests were continued for x-x days (160-270 pore volumes), during which time varying degrees of saturation were maintained in the columns by manipulating the elevation of the outlet tubing. During saturated flow conditions, relatively high concentrations of PO_4 were eluted from the Cambridge and Langton high P zones (up to 4 and 9 mg L-1 P, respectively), accompanied by elevated concentrations of Fe (up to 1.4 mg L-1) and Mn (up to 4 mg L-1) and lower values of Eh (< 150 mv). The 'Below' zones at Cambridge and Langton however, maintained lower concentrations of P (generally < 2 mg L-1), Fe (<0.2 mg L-1) and Mn (< 1 mg L-1) and maintained higher Eh (> 250 mv) during saturated flow conditions. During unsaturated flow, P and

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Fe declined dramatically in the high P zones (P < 1mg L-1. Fe < 0.2 mg L-1), whereas concentrations remained about the same as during saturated flow in the 'Below' zones. This behavior is attributed to the development of reducing conditions during saturated flow in the high P zones, leading to reductive dissolution of Fe (III)-P solids present in the sediments. Reducing conditions did not develop in the 'Below' zones apparently because of lower sediment organic carbon contents (0.03-0.04 wt %) compared to the high P zones (0.2-0.65 wt%). At the Muskoka site, where the sediments were noncalcareous. low values of P (<0.2 mg L-1) were maintained throughout.

Results indicate the possibility of remobilizing P minerals precipitated below septic system infiltration beds should more reducing conditions develop. This could occur if sewage loading patterns change, for example when a lakeshore seasonal use cottage is converted to a permanent dwelling.

1. Introduction

The low concentrations at which phosphorus can stimulate algae growth in aquatic environments (~30 ug/L, Dillon and Rigler, 1974; Schindler, 1977) compared to the approximately 300 times higher concentrations in wastewaters such as sewage, leads to concern when sewage is discharged near surface water environments. Of particular concern is the use of septic systems near lakeshore environments, because phosphorus control measures normally employed with larger wastewater treatment systems (eg. reagent dosing with alum, lime, ferric chloride, etc), are rarely used with small onsite

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treatment systems because of the added costs and maintenance associated with sludge handling. Phosphorus control in most septic systems relies largely on natural subsurface attenuation. However, regulated setback distances from lake shorelines are often small (e.g. 15m, Province of Ontario) and loading occurs over long periods, thus some jurisdictions have chosen to adopt a conservative approach and assume, that over time, natural attenuation (i.e. adsorption) is exhausted and downgradient migration of P will ensue (e.g. Dillon et al. 1986). Under this assumption septic systems can represent the largest source of P loading to some lakes (e.g. up to x% in Ontario lakes, Dillon et al. 1986).

Recent studies of P behaviour in septic system plumes however, have failed to confirm that natural attenuation diminishes during long term loading. On the contrary, these investigations have generally shown that even when septic systems have been in operation for decades, substantial P attenuation still occurs in close proximity to the infiltration pipes. In a recent review of 10 mature septic system plumes, Robertson et al. (1998) found that 25-99% of the sewage P mass was still attenuated within 1-3m of the infiltration pipes even though all of these systems had been in operation for more than 10 years. Clearly, such behaviour requires attenuation based on mineral precipitation reactions rather than adsorption. This distinction is fundamentally important as it implies that the attenuation reactions are potentially sustainable. Further evidence of mineral precipitation dominated P attenuation was presented by Zanini et al. (1998) who revealed the presence of distinct narrow layers of P enrichment in the vadose zone sediments below these septic system infiltration beds (Fig. 1). These layers appeared to coincide with the redoxcline, the horizon representing the zone of most intense sewage oxidation. Two primary attenuation reactions were proposed: 1) in noncalcareous terrain, the

development of acidic conditions, followed by gibbsite (Al(OH)$_3$) dissolution and subsequently variscite (ALPO$_4$ · 3H$_2$O) precipitation and 2) the conversion of ferrous iron (FeII) to ferric iron (FeIII) and the subsequent precipitation of sparingly soluble ferric minerals such as strengite (FePO$_4$ · 3H$_2$O). Scanning electron imaging and microprobe analyses confirmed that P occurred as distinct authogenic coatings on primary sediment grains and as distinct secondary grains (Fig 2). Furthermore, Al and Fe were the dominant cations occurring in association with these P minerals (Fig 2). Thus, under these circumstances. it can be argued that the P attenuation reactions are sustainable, provided that existing redox conditions are maintained and a supply of cations remains available, either from the sewage effluent or from the sediments.

The assumption of a sustained redox environment below a septic system tile bed is perhaps open to question, however. Changes in water usage patterns. as for example when a seasonal use residence is converted to a full time dwelling, might cause the redoxcline to migrate downward increasing the possibility of intercepting the water table. Should conditions become more reducing, the fate of P minerals previously precipitated at the oxidation front, is currently uncertain. A number of examples are available to suggest however, that secondary ferric (FeIII) minerals become unstable and dissolve when subjected to reducing conditions These include, examples from mine tailings environments (Ribet et al. 199?), natural flowsystems (Lovely and Phillips 1986), landfill leachate plumes (xxx, 2000) and wastewaters interacting with natural sediments (Robertson, 2000).

In the present study, the geochemical stability of septic system- derived P solids is evaluated under conditions of changing redox environment. A series of laboratory

column studies were undertaken using the same subtile sediment cores characterized previously by Zanini et al. (1998). These include cores from the Cambridge, Langton and Muskoka sites where detailed field investigations were undertaken beginning in 1987, investigating septic system plumes (e.g. Robertson et al. 1998). At all three sites, septic systems have been in operation for more than 10 years, servicing single family households at Muskoka and Cambridge and a public school with ~300 students at Langton. In each case the tile bed is located on an unconfined sand aquifer with water table depth at 2-3 m. At Cambridge and Langton the aquifer sands are calcareous (5-32 wt% $CaCO_3$ equiv.), while at Muskoka the aquifer is noncalcareous (<1.0 wt% $CaCO_3$ equiv) and acidic conditions (pH ~ 4.5) have developed in the plume. Cores retrieved from below the tile beds at these three sites, revealed the presence of distinct layers of P enrichment immediately below the tile lines. These occurred within 1 m of the infiltration pipes and were enriched in total P (TP) by a factor of 2-4 compared to overlying and underlying sediments (Fig. 1). SEM images and microprobe compositional analyses showed that the P minerals occurred as authigenic grains and coatings with Fe as the primary cation at Cambridge and Langton and Al as the primary cation at Muskoka (Fig. 2).

Although a number studies have assessed P behaviour during sediment-water interaction under changing redox conditions (Sah and Mikkelson, 1986; Moore and Reddy, 1994; among others, p.s. add another here if appropriate), this is the first study we are aware of that directly uses tile bed sediments containing secondary P solids. Although the general composition of the P minerals have been established (Zanini et al. 1998; Ptacek and Pratt, 1998), their exact mineralogy has not. It is likely that a variety

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of minerals are present, including solid solutions between various end members. Many of these have limited solubility information available. It is thus difficult to predict the solubility and redox behaviour of these P solids, a priori, without direct evaluation.

2. Methods

2.1 Core Collection

Sediment cores were retrieved from below the tile bed areas in 1994 using a percussion hammer and 5 cm dia. aluminum core tubes. At each site, one to four continuous, undisturbed cores were collected through the vadose zone to 2-3m depth. Cores were segmented into 0.1-0.3m intervals, capped and stored in the dark at room temperature. Selected cores were then subsampled for analysis of TP content at 2-5 cm increments. Detailed core handling and sampling procedures are described by Zanini et al. (1998).

2.2 Column Tests

Sample splits, from the same cores used previously by Zanini et al. (1998), were used to conduct dynamic flow column tests. Six detailed tests were carried out, each using ~150g of remixed sediment from 0.1-0.3 m long core intervals. Two tests were carried out per site, targeting intervals from within and below the zones of P enrichment (Fig. 1). Sediments were packed to a height of ~17 cm in 2.5 cm dia. plexiglass columns, fitted with drainage tubes at the bottom. Testing was undertaken by dosing the columns from the top, using a peristaltic pump and timer, after which the effluent was allowed to drain out the bottom through the drainage tube. Varying conditions of

saturation were established by positioning the discharge tube elevation either above or below the bottom of the column. All of the sediments utilized were fine-coarse sands with relatively minor silt+clay content (<7 %, Table 1). The air entry pressure of the sediments *were* estimated from the grain size characteristics using the relationship of Nicholson et al. (1991), or *were* measured directly by observing the onset of drainage upon lowering the position of outlet tube. The physical and chemical properties of the sediments are given in Table 1 and their drainage characteristics are presented in Table 2.

Influent solutions used in the tests were either calcite-saturated deionized water for the two calcareous sites (Cambridge and Langton), or unamended deionized water for the noncalcareous site (Muskoka). Changes in redox conditions were accomplished by manipulating the elevation of the outlet tubing which subsequently affected the degree of water saturation and air-filled pore space in the column sediments. Unsaturated conditions were established generally by positioning the outlet tubing below the columns, a distance in excess of the Air Entry Value (> 28-62 cm). Water contents were measured periodically during the tests, by comparing column operating weights to their original dry weights. In addition, effective water filled porosities were established at the end of the tests, by conducting tracer tests in which the influent solution was spiked with NaCl and then changes in effluent electrical conductivity (EC) were monitored with a portable meter.

The column tests were run for a period of 170-260 days (pore volumes?) at loading rates generally in the range of 27-34 ml/day. The daily loading rates were selected to be approximately equivalent to the saturated effective pore volumes indicated from the tracer tests (Table 2) (p.s. or was it saturated water content measured

gravimetrically?). However, pump limitations did not allow loading to be adjusted precisely for each column, as loading occurred simultaneously (3-4 columns at once) using a multihead peristaltic pump. During the Muskoka and Cambridge tests, the loading rate was temporarily reduced by one half (27-34 ml every second day) during pore volumes 76-130, (p.s. here is potential confusion, is this really pore volumes or is it time? hopefully it is pore volumes) to demonstrate the effect of longer hydraulic retention times on the release of P. Thus, retention times in the columns were in the range of 24-48 hr during saturated flow conditions and were marginally less during unsaturated flow conditions because of the slightly lower water contents (4-13% lower, Table 2) at that time.

2.3 Sampling

Effluent was collected in 30 ml PET syringe barrels (and volumes recorded?). Samples were retrieved directly from the container or from a flow-through cell attached to the outlet tubing, which allowed sample collection prior to atmospheric exposure. Measurements of Eh were obtained using the a flow through cell and a portable meter (Barnant model ...) with Ag/AgCl reference electrode checked against Zobell's solution (Nordstom, 1977). Measurements of pH were made after decanting ~ 10 ml of effluent into the syringe barrel, using $\frac{1}{2}$ the same meter with a combination electrode calibrated a,a,... using buffers of pH 4 and 7. Samples for ion analyses were filtered (0.45 um) and acidified with 6N H_2SO_4 to pH < 2 immediately after collection and were stored at ~4° C in 20-60 ml plastic containers until analysis. Phosphate (PO_4) content was measured by the ammonium molybdate/ascorbic acid method (Standard methods, 1992) which

provided a lower detection limit of 0.01 mg L-1 P or by the ? method (ref) which provided a lower detection limit of 0.05 mg L-1 P. Fe and Mn were measured by ICP-OES analysis (USEPA Method 200.7) which provided a detection limit of 0.1-0.2 mg L-1 for Fe, and 0.05 mg L-1 for Mn, or by atomic adsoption spectophotometry (Varian Model 1475 Atomic Adsorption Spectrophotometer) which provided a dection limit of 0.05 mg L-1 for both Fe and Mn. Al was measured by inductively coupled plasma – mass spectrometry (ICP-MS) analysis (USEPA Method 200.7), which provided a lower detection limit of 0.01-0.02 mg L-1. Sediment total P content was measured using the ? method (ref). Sediment NaHCO₃ extractable P was measured using the ? method (ref).

3. Results

Figures 3-5 show the breakthrough of PO₄, Fe, Mn, Al and Eh in the column effluent over the duration of the tests. For simplicity, the time scale is normalized with respect to the effective saturated pore volumes determined from the tracer tests (19-31 ml, Table 2) (p.s. is this statement correct or not?). Note however, that the column tests also included periodic unsaturated flow conditions (Figs 3-5), during which the effective pore volume was probably less than the saturated value. This would result in underestimation of the number of pore volumes, however this effect was probably minor because the decrease in water content during unsaturated flow was relatively small (4-14 %, Table 2).

p.s. Myron; I'm not sure I follow your editorial comments here but the above qualifier is included to hopefully defuse this situation. I'm still not really clear how you defined

'pore volume' in each case. Was it a single value or a moving target? (also qualifier statement is now included in methods section).

Concentrations of PO_4 and Fe varied considerably during testing from values below detection, to up to 9 mg L-1 P for PO_4 and 1.3 mg L-1 for Fe. During unsaturated flow conditions, PO_4 and Fe values were generally similar to the site plume values (PO_4 P, 0.5-4 mg L-1 at Cambridge and Langton and <0.1 mg L-1 at Muskoka; Fe <0.3 mg L-1). However, during saturated conditions in the Cambridge and Langton high P columns, effluent Eh decreased significantly to +50 to +100 mV and P and Fe concentrations increased substantially by a factor of about 3 for P (4-9 mg L-1) and by a factor of 5-10 for Fe (1.0-1.3 mg L-1, Figs 3 and 4). These values substantially exceeded plume values for PO_4 at Langton (1-2 mg L-1) and for Fe at both sites. Fe and P increases during saturated conditions, were much less apparent however, in the 'Below' columns at both Cambridge and Langton.

The Muskoka columns, in contrast, maintained low effluent PO_4 P and Fe (<0.1 mg L-1), and high Eh (>300 mV) under all experimental conditions.

It should be noted that the test intervals indicated as 'unsaturated' on Figures 3-5 represent only partial drainage of the column sediment (4-14%, Table 2). This was because the outlet tube elevation, during these periods, was generally positioned close to the air entry value for the sediment, but did not always substantially exceed it. Nonetheless, using the relationship of Reardon and Moddle (1985), the modest amount of drainage achieved would have increased air diffusivity in the column sediments by a factor of 6-400 (Table 2), which was apparently sufficient to substantially alter the redox environment of the columns.

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4. Discussion

In the Cambridge and Langton columns, the abrupt increases in Fe and Mn coincide

with declining Eh, providing strong evidence that reductive dissolution of Fe(III) solids is

occurring. Coincidental increases in P suggest that P adsorbed onto these Fe(III) solids,

or contained as part of their mineral structure, is also being released. Examination of the

P mass eluted from the columns (Table 4) however, shows that at both Cambridge and

Langton. the total P mass eluted (8-145 ug/g). substantially exceeds the readily

desorbable amount (NaHCO$_3$ extractable fraction) that was consumed during testing (0-

19 ug/g), suggests that much of this P mass was derived from mineral dissolution. This

behavior is consistent with the previous characterizations by Zanini et al. (1998), which

showed P occurring primarily with Fe in secondary coatings and grains at these two sites

(Fig. 2). The lack of PO$_4$ redox response at Muskoka is also consistent with the

mineralogical evidence, which shows P occurring predominantly with Al, a cation that

occurs exclusively in the +3 valence and is not redox sensitive.

Reduction of Fe(III) to Fe(II) requires an energy source (electron donor). This

source was not rigorously established during these tests, but is presumed to derive from

the column solids. It is noted that the sediment organic carbon contents (foc) are

enriched in the P rich zones, by a factor of 7-10 compared to the 'Below' sediments, at

both Cambridge and Langton (Table1). Presumably much of this excess organic carbon

is relatively labile, sewage-derived carbon that could act as an energy source for

reductive dissolution of the ferric solids. In support of this, is the apparent absence of

reductive dissolution in the 'Below' zones where foc is much less. Presumably much of

Likely

the added foc in the high P zones is particulate material that was removed by physical filtration within a few 10's of centimeters of the infiltration pipes and is thus not present in the deeper sediments.

5. Implications

In situations where phosphorus is retained in association with Fe(III) solids, a situation that appears common below septic system tile beds, vulnerability to remobilization appears to exist should a change in redox conditions occur. The normal aging of a tile bed may, in some cases, lead to gradual plugging of the pore space around the tile lines leading to diminished diffusive influx of atmospheric oxygen and the subsequent onset of more reducing conditions. This may not always occur however, as both Cambridge and Langton provide examples of tile beds that have operated successfully for very long periods (23 and 44 years respectively) without any indication of deteriorating redox conditions.

Sites that experience increased sewage loading may be more at risk. Examples include lakeshore cottages that were used initially only during the summer months, but are then converted to permanent residences, resulting in increased loading, including loading during potentially higher water table conditions in the Spring and Fall months. On the other hand, sites on noncalcareous terrain, where P is retained in association with Al minerals, may be less at risk of redox-induced remobilization of P.

6. References

(cull from Zurawsky, 2000)

Table 1. Properties of sediments used in the column experiments.

Core		Depth (m)	Silt+Clay[1]	Sand[1] (wt%)	CaCO$_3$[2]	foc[2]	d$_{10}$ (mm)	TP[1] (ug/g)	Fe[2] (ug/g)
Cambridge: High P	UG33	0.64-1.00	2	98	20	0.65	0.14	650	15300
Below	UG33	1.15-1.30	3	97	32	0.06	0.12	110	8200
Langton: High P	LAM310	1.18-1.45	7	93	5	0.2	0.10	815	16930
Below	LAM310	1.67-1.89	5	95	<1	0.03	0.12	341	7230
Muskoka: High P	MM420	0.56-0.74	7	93	<1	not meas.	0.09	350	29500
Below	MM420	1.17-1.27	4	96	<1	0.04	0.11	330	25100

1. from Zurawsky (2000)
2. from Zanini (1996)

Table 2. Column characteristics

	Cambridge		Langton		Muskoka	
	High P	Below	High P	Below	High P	Below
Sed dry wt (g)	146	153	128	127	153	158
Pore Volume[1] (cc)	31	30	21	27	19	31
Effective porosity[1] (%)	36	34	28	36	23	36
Water content[2]: sat (%)	48	47	39	36	41	46
unsat (%)	34-42	34-41	27	28-32	33-34	34-38
Air dif[3] (cm^2/s x10^{-5}): sat	1	1	1	1	1	1
unsat	9-400	9-300	200	6-60	60	60-200
AEV; estimated[4] (cm)	43	50	58	50	62	54
measured (cm)	49	54			28	29

1. Saturated effective pore volume or porosity determined from tracer tests
2. determined gravimetrically
3. air diffusivity estimated from air filled porosity using relationship of Reardon and Moddle (1985)
4. air entry value estimated from d$_{10}$ grain size using relationship of Nicholson et al. (1991)

p.s. Myron; I'm not sure I follow your editorial comments with regard to the water contents in this table. It needs to remain simple and therefore must avoid the saturated vs

tension saturated controversy as much as possible. The only real issue is saturated vs unsaturated. Saturation should be considered the maximum water content you measured during testing, anything less is unsaturated. The ambiguity/confusion regarding tension saturation, I think is now adequately addressed by the new headers on Figures 3-5 which specify water contents. If you think more clarification is needed on this table, I would suggest adding additional footnotes.

p.s. 2 . Are there measured AEV values available for Langton and Muskoka?

Table 3. Representative column effluent chemistry and mineral saturation indices. (Myron/Carol)

Table 4. Comparison of P content in the column sediments before and after the column tests (average of 1-3 analyses from Zurawsky, 2000).

	Cambridge				Langton				Muskoka		
	High P		Below		High P		Below		High P		Below
	before	after	before	after	before	after	before	after	before	after	before
Total P (ug/g)	650	580	110	243	815	997	341	312	350	401	330
NaHCO₃ (ug/g)	58	45	11	11	81	75	49	30	2	2	3
P eluted (ug/g)		68		8		145		107		<2	

Fig. 1. Profiles of solid phase P below 3 septic system infiltration beds (adapted from Zannini et al. 1998) and core intervals used for the column tests.

Fig. 2. Back-scattered electron images and microprobe elemental analyses of representative P solids from the three study sites (adapted from Zanini et al. 1998).

Fig. 3. Cambridge site (calcareous) column effluent: a) PO_4, b) Fe, c) Mn, d) Al and e) Eh.

Fig. 4. Langton site (slightly calcareous) column effluent: a) PO_4, b) Fe, c) Mn, d) Al and e) Eh.

Fig. 5. Muskoka site (noncalcareous) column effluent: a) PO_4, b) Fe, c) Mn, d) Al and e) Eh.

Lovely, D. R., and E.J.P. Phillips. 1986. Organic matter mineralization with reduction of ferric iron in anaerobic sediments. Appl. Environ. Microbiol. 51: 683-689.
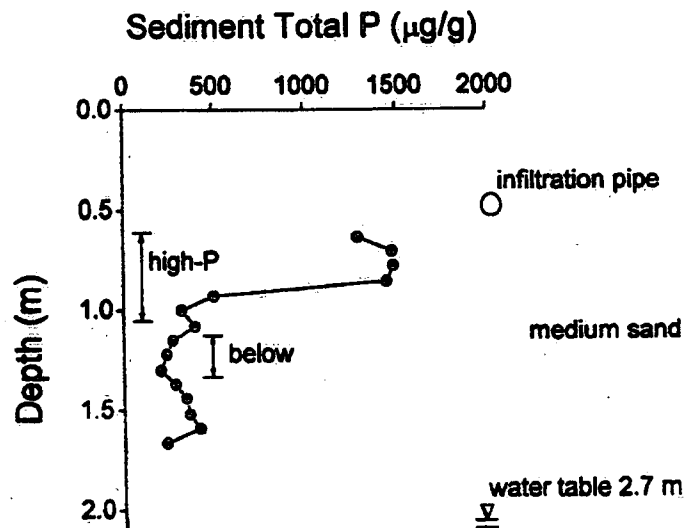
Ptacek and Spratt, 1998. ....Carol

Ribet et al. 199?.........Carol

Landfill 2000...........Carol

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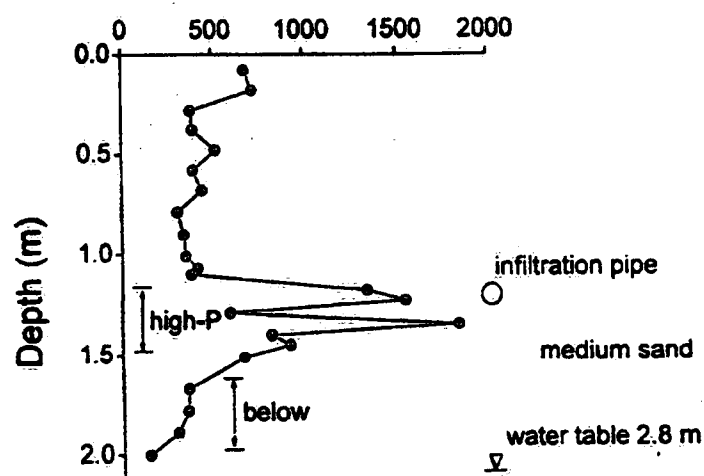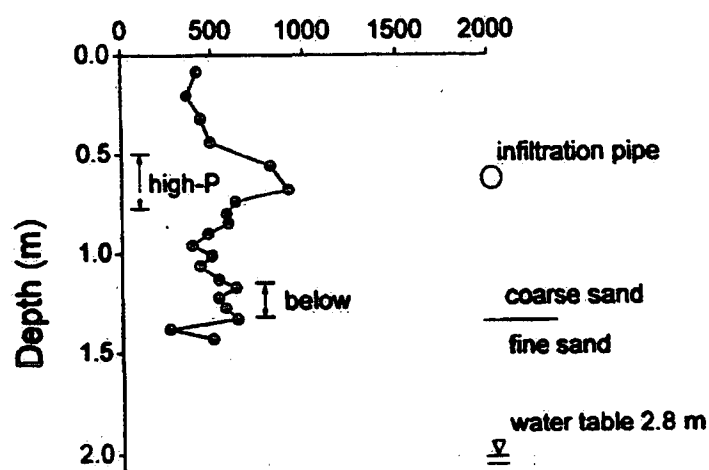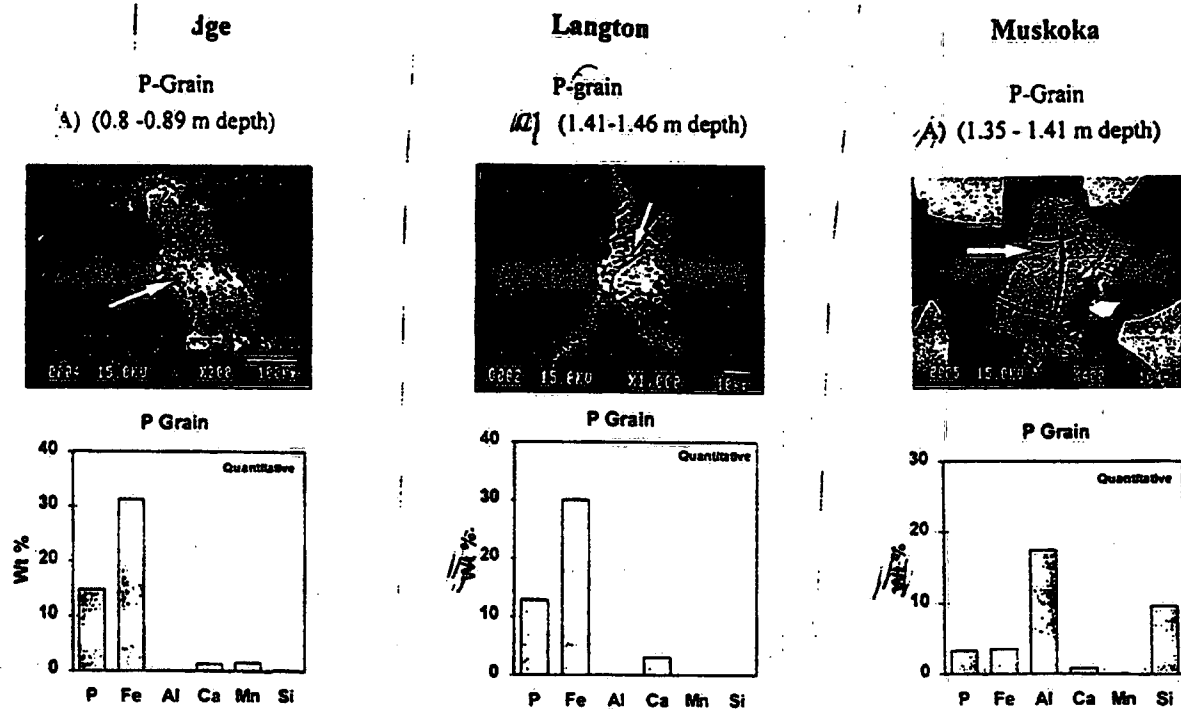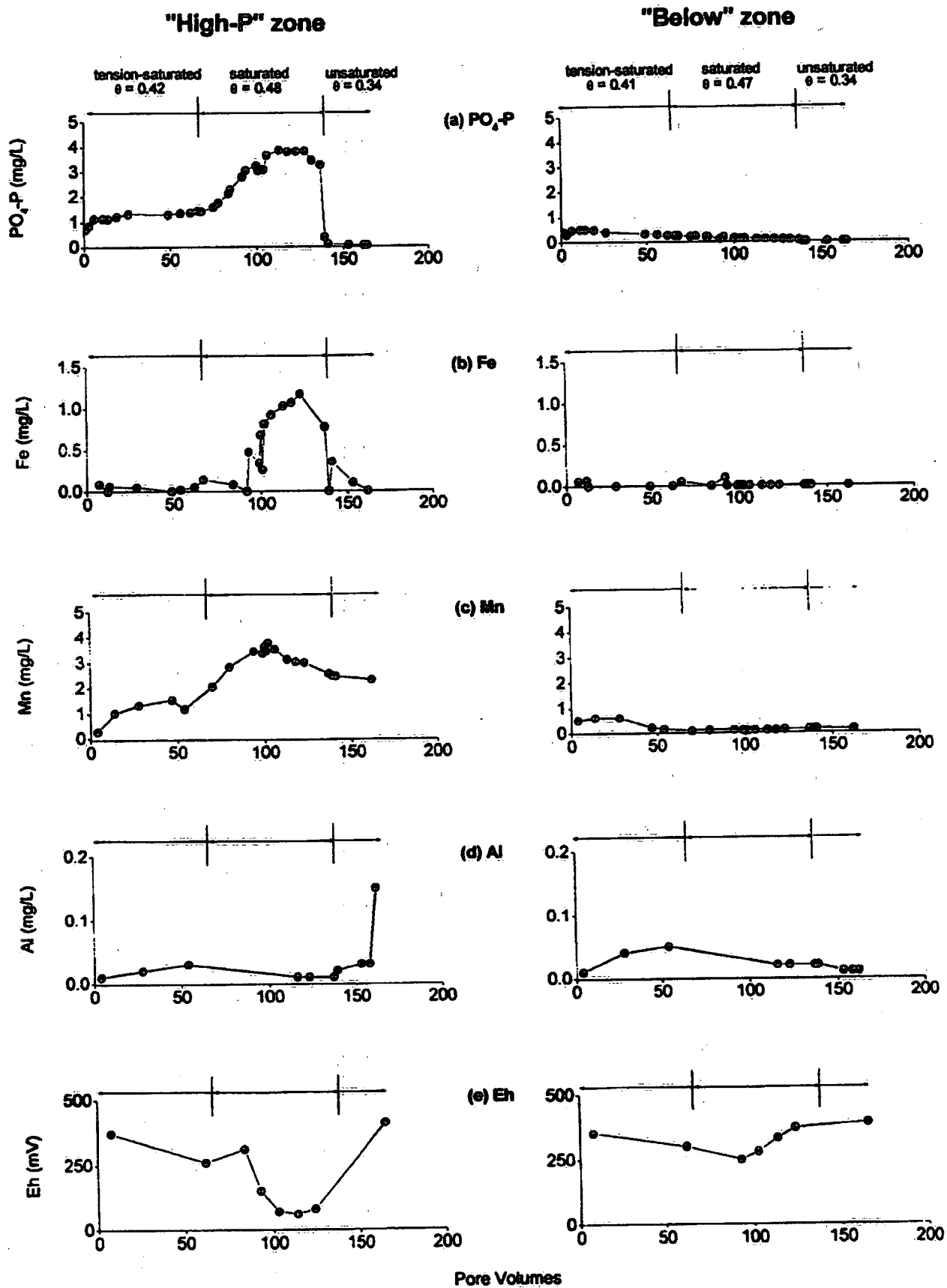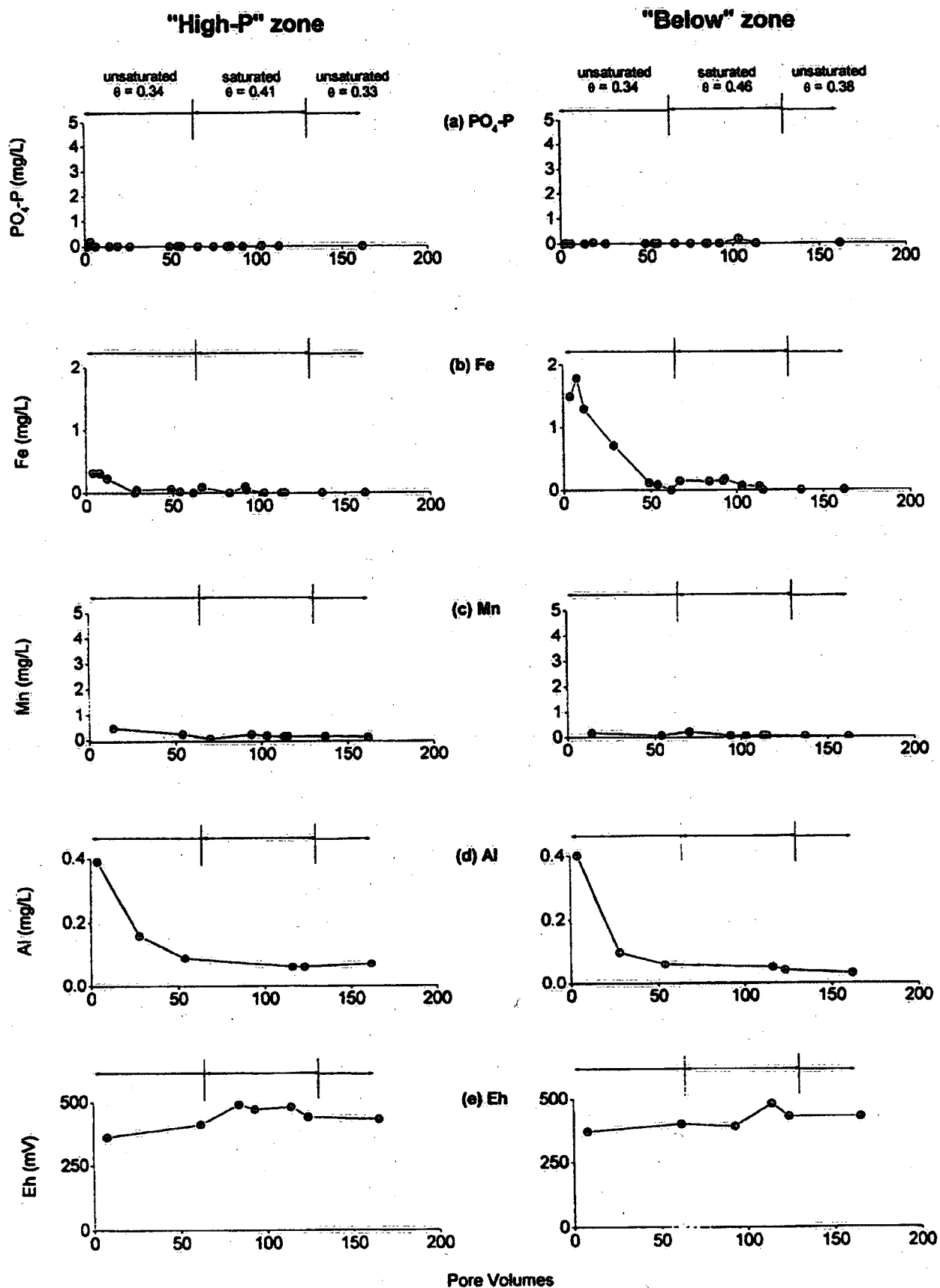
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"High-P" zone

"Below" zone
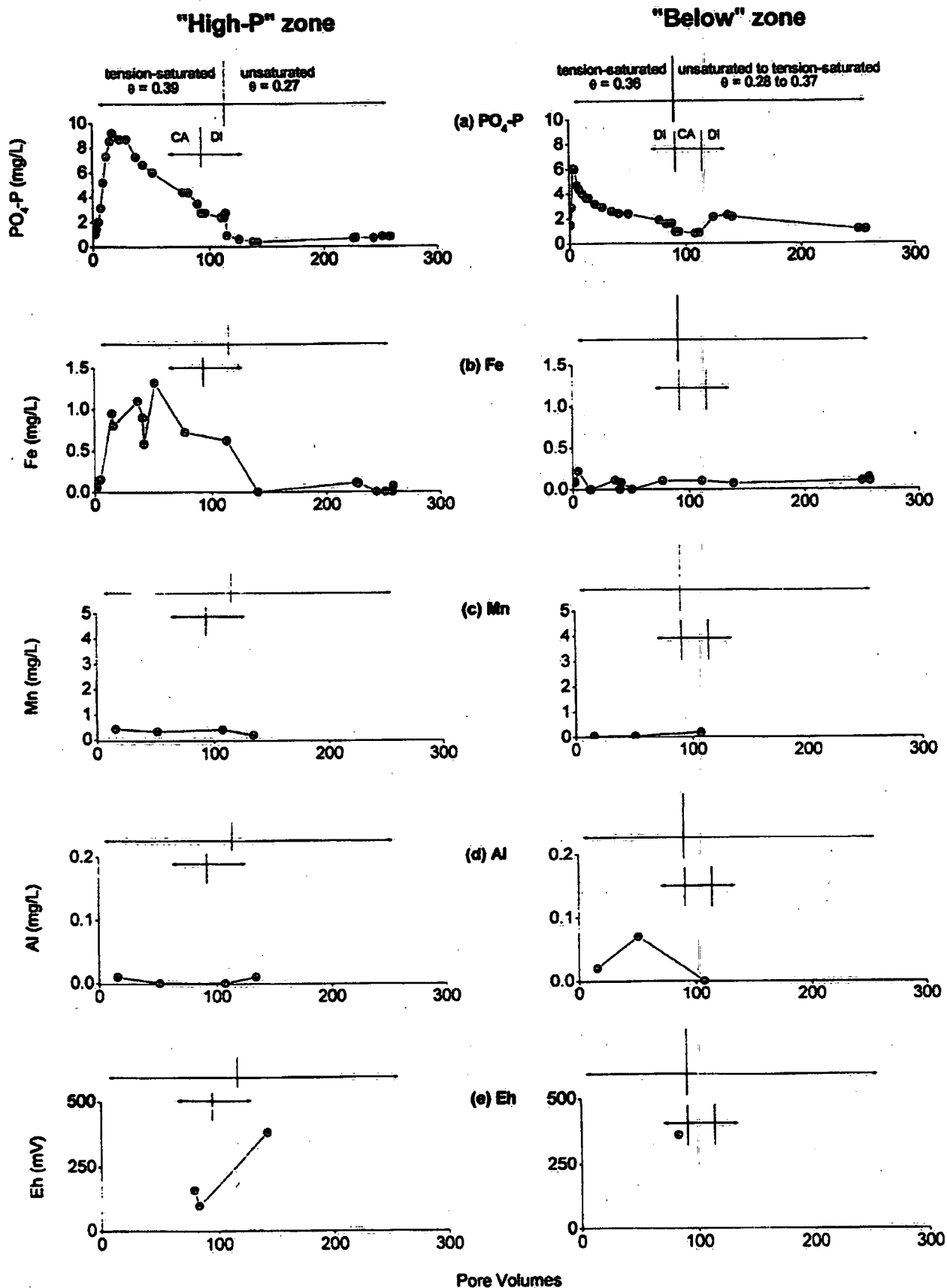
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