# OCCURRENCE OF PHOSPHATE IONS IN LOESS SOILS[*]

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Abstract. In model experiment (anaerobiosis) with full saturation of soil samples with water and their incubation at 5, 10 and 20°C during 0-60 days, phosphate ions ($PO_4^{-3}$) concentration in soil solution, Eh and pH in soil sediment were determined. For the investigations 12 samples from loess soils representing surface-humus horizons were taken from various parts of 4 eroded slopes in a small river catchment near Lublin, Poland. Differentiation in $PO_4^{-3}$ concentration in the range of 0.18-2.10 mg dm$^{-3}$ was found, depending on the temperature and time of soil samples incubation and also on the place of sampling.
Keywords: phosphate ions, Eh, pH, loess soils, anaerobic conditions

## INTRODUCTION

Plant nutrients are positively evaluated if retained in the soil for uptake by plants, but become environmental pollutants if leached into surface and subsurface waters (McGechan and Lewis 2002). Much attention has been devoted to nitrogen as a nutrient and pollutant due to its high solubility, leachability and volatility from soils. Less attention has been paid towards the less soluble and non-volatile contaminating plant nutrient – phosphorus. High phosphorus input to the aquatic environment, resulting in eutrophication of lakes, rivers and reservoirs, is still a major problem of water management in most European countries (Olila 1996, Gelbrecht *et al.* 2005). Eutrophication is arguably the biggest pollution problem facing estuaries globally, with extensive consequences including anoxic and hypoxic waters, reduced fishery harvests, toxic algal blooms, and loss of biotic diversity (Howarth *et al.* 2000).

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The factors which may regulate phosphorus reactivity in inundated soils include redox potential and pH (Tiedje *et al.* 1984, Gliński and Stępniewski 1985, Stępniewska 1988, Shahahandeh *et al.* 1994, Gardolinski *et al.* 2004).

Phosphorus (P) is a nonmetallic chemical element. It is not found free in nature and is always present in the form of phosphates, creating with cations orthophosphate salts (Yu Tian Ren 1985).

Phosphorus is an essential element for the growth and development of living organisms. Its natural sources in soils are phosphate minerals, mainly apatite, wavelite and vivianite. In well-developed soils, most of the phosphorus is combined with organic matter (in living and dead plants, animals, insects and microorganisms). In agriculture phosphorus refers to one of the three primary plant nutrients (N,P,K) and it is a component of fertilizers. Plants take up P in smaller amounts than N or K, on average at the ratio N:P:K = 2.2:0.4:2.0. The concentration of P in the plant xylem is 100- to 1000-fold higher than in the external soil solution (Sapek and Sapek 2004). Total soil P ranges from 0.01 to 0.30%. It is almost entirely associated with soil colloidal particles, either inorganic or organic.

A certain amount of P in soils results in an increase of its level in soil solution followed by an increase of P amount in water that passes through the soil profile. Inorganic P is usually associated with Al, Fe or Ca compounds of varying solubility and availability to plants. It can be rapidly fixed in unavailable forms, depending on soil pH and Al, Fe and Ca contents. The influence of Eh on the changes of P is not direct, but its solubility is connected with changes of Eh through phosphorus precipitation with elements such as Fe and Mn ions (Engels *et al.* 1995, Kirk and Saleque 1995, Olila 1996). Generally, the solubility of P for plants is optimal at pH in the range 6.5-7.0 (Sime and Vadas 2005).

Phosphorus transfer from soils to water bodies is a major non-point source of pollution. This transfer is due to processes of leaching, erosion, and surface run-off and also with subsurface water flow to nearby streams, especially if artificial drainage is present. Phosphorus can be transported either as soluble P in runoff water or as P adsorbed to eroding soil particles. It results in the elevation of the bioavailable P and leads to eutrophication of the waters (Gliński and Dębicki 1999).

Phosphates are the naturally occurring form of the element phosphorus. In dilute aquatic solution, phosphates exist in four forms. In strongly basic conditions, the phosphate ions ($PO_4^{-3}$) predominate, while in weakly basic conditions, the hydrogen phosphate ions ($HPO_4^{-2}$) are prevalent. In weakly acid conditions, dihydrogen phosphate ions ($H_2PO_4^{-}$) are the most common. In strongly acid conditions, aquaeous phosphoric acid ($H_3PO_4$) is the main form (Sime and Vadas 2005). The phosphate ions are polyatomic ions with a molecular mass of 94.97 daltons. They carry a negative three formal charge.

The purpose of this paper was to show, in a model experiment, the possibility of $PO_4^{-3}$-P occurrence in arable loess soils.

## MATERIALS AND METHODS

The object of the study was an eroded loess slope at 4 localities (Motycz, Snopków, Baszki and Pliszczyn) near Lublin, along the Ciemięga river catchment. The catchment is located on 200-230 m a.s.l. and covers an area of 157 km$^2$. It length is 41 km. The first two localities (Motycz and Snopków) are situated in upper part of the catchment which is of gentle relief. The two others (Baszki and Pliszczyn) characterize the lower part of the catchment with strong undulating relief. The soils (*Haplic Luvisols* and *Eutric Cambisols*) are formed of typical silty deposits of loess containing, in their upper horizons, 1.74-5.42% of organic matter, with specific surface area of 31.84-70.95 m$^2$ g$^{-1}$, pH 6.6-8.1 and $PO_4^{-3}$-P from 0.06 to 2.84 mg dm$^{-3}$ in soil solution at 20°C (Tab. 1). Samples for all investigations were taken during the Spring, the Summer and the Autumn 2003 in three replications after cereals.

For the investigations, 12 samples were taken from three places on the slopes (upper part-1, middle part-2, and lower part-3) of 4 localities (Motycz – M, Snopków – S, Baszki – B, Pliszczyn – P). They represented surface-humus (0-20 cm) horizons. Soil samples were placed in glass vessels, flooded with distilled water at the ratio of 1:2.5 (15 g soil+37.5 cm$^3$ water), covered and incubated at 5, 10 and 20°C. In the course of incubation, at different time intervals (days), $PO_4^{-3}$ concentration in soil filtrates was measured. The following methods were used to analyse the soil filtrate:

Redox potential and reaction were measured in soil suspension. Redox potential measurements were made using a calomel electrode as the reference electrode with constant non-zero potential, well tested and accurately calibrated with relation to the standard hydrogen electrode (Gliński and Stępniewska 2005). Redox measurements were taken using an "pIONneer 10" Radiometer portable apparatus.

Reaction (pH) – the measurement was performed by a combined electrode using Radiometer pH Meter.

Determination of $PO_4^{-3}$-P concentration was performed with the help of the FIA-Star 5010 flow-through spectrophotometric analyser made by Foss Tecator (Application Note ASN 60-01/83, 1983). Determination of $PO_4^{-3}$-P was made according to the following method: the sample containing ortho-phosphate reacted with ammonium molybdate to form heteropoly molybdophosphoric acid. The acid was reduced in a second step to dissimilative path reductases which use $NO_3^-$-N as electron acceptors alternative to $O_2$.

**Table 1.** Grain size composition and some properties of examined soils

| Locality | Place on slope | Grain size composition (% of fraction in mm) | | | | | | O.M. (%) | $S_{H_2O}$ (m$^2$ g$^{-1}$) | $S_{N_2}$ (m$^2$ g$^{-1}$) | $PO_4^{-3}$-P (mg dm$^{-3}$) | pH $_{H2O}$ |
| | | 1-0.1 | 0.1-0.05 | 0.05-0.02 | 0.02-0.005 | 0.005-0.002 | <0.002 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Motycz (M) | Upper(1) | 27 | 12 | 35 | 13 | 3 | 10 | 1.74 | 35.07 | 7.06 | 0.14 | 6.6 |
| | Middle(2) | 10 | 13 | 46 | 20 | 4 | 7 | 1.87 | 31.84 | 6.39 | 0.06 | 7.5 |
| | Lower(3) | 8 | 12 | 48 | 20 | 7 | 5 | 5.42 | 70.95 | 8.63 | 0.34 | 7.4 |
| Snopków (S) | Upper(1) | 7 | 15 | 56 | 3 | 17 | 2 | 3.08 | 47.24 | 6.80 | 2.84 | 7.9 |
| | Middle(2) | 6 | 14 | 57 | 17 | 2 | 4 | 2.40 | 40.93 | 9.53 | 2.26 | 7.7 |
| | Lower(3) | 22 | 18 | 50 | 7 | 1 | 2 | 5.08 | 55.69 | 6.65 | 1.21 | 7.9 |
| Baszki (B) | Upper(1) | 6 | 9 | 53 | 21 | 3 | 8 | 2.28 | 36.78 | 15.31 | 0.18 | 8.1 |
| | Middle(2) | 4 | 13 | 50 | 20 | 5 | 8 | 1.94 | 40.44 | 10.88 | 1.01 | 7.1 |
| | Lower(3) | 8 | 14 | 58 | 13 | 2 | 5 | 2.72 | 35.36 | 8.97 | 0.92 | 7.6 |
| Pliszczyn (P) | Upper(1) | 1 | 10 | 62 | 19 | 1 | 7 | 2.63 | 40.58 | 12.35 | 0.07 | 7.5 |
| | Middle(2) | 8 | 12 | 53 | 19 | 1 | 7 | 2.51 | 33.72 | 6.61 | 0.07 | 7.8 |
| | Lower(3) | 13 | 15 | 47 | 19 | 1 | 5 | 3.48 | 34.70 | 5.25 | 1.01 | 8.1 |

O.M. – Organic matter, $S_{H_2O}$ – specific surface area measured with $H_2O$ adsorption – $S_{N_2}$ – specific surface area measured $N_2$ adsorption

The chosen conditions of long lasting full water saturation of loess soils at various temperatures appear in the south-east of Poland.

Analysis of variance by the least significant difference test (95% LSD-test) was performed to determine whether a significant difference existed ($p < 0.05$) between means of locality, means of temperature and means of place on slope at different temperatures.

## RESULTS

Mean phosphate ions concentration (from the sum of all 204 treatments) was 0.84 mg dm$^{-3}$ at mean values of Eh 298 mV and pH 7.2 (Tab. 2).

Taking into consideration the places of soil sampling in 4 localities (M, S, B, P) along the catchment, the highest phosphate ions concentration in soil solution was found in S (2.10 mg dm$^{-3}$) compared to the other localities (0.18-0.70 mg dm$^{-3}$) (Fig. 1).

Probably in this location fields got more P fertilizers. Eh values were higher in the lower part of the catchment (318 mV and 303 mV) and lower (292 mV and 281 mV) in the higher part of the catchment (Tab. 2).

**Table 2.** Mean values of phosphate ions (PO$_4^{-3}$-P), Eh (redox potential), pH and temperature of soil samples coming from different localities and places on the slope

| | Stand | PO$_4^{-3}$-P (mg dm$^{-3}$) | Eh (mV) | pH |
|---|---|---|---|---|
| | All results (n = 204) | 0.84 | 298 | 7.2 |
| Locality | M (n = 51) | 0.18 | 292 | 6.6 |
| | S (n = 51) | 2.10 | 281 | 7.3 |
| | B (n = 51) | 0.70 | 318 | 7.1 |
| | P (n = 51) | 0.38 | 303 | 7.6 |
| Slope | 1 (n = 68) | 0.81 | 322 | 7.4 |
| | 2 (n = 68) | 0.85 | 311 | 7.6 |
| | 3 (n = 68) | 0.87 | 262 | 7.4 |
| Temperature | 5$^o$C (n = 84) | 1.16 | 305 | 7.4 |
| | 10$^o$C (n = 72) | 0.50 | 283 | 7.3 |
| | 20$^o$C (n = 48) | 0.79 | 309 | 7.0 |

Soil reaction (pH) was fairly equal (7.1-7.6 for S, B and P) except for the lower value (6.6) for M in the upper, less eroded, part of the catchment where upper horizons were farther from loess deposits with basic reaction (Tab. 2).

A significant differentiation appeared in phosphate ions concentration in soil solution with relation to temperature (Fig. 2).

A tendency of increasing phosphate ions concentration in soil solution going from the upper to the lower parts of slopes (0.81, 0.85 and 0.87 mg dm$^{-3}$) (Fig. 3) and an opposite trend concerning Eh values (322, 311 and 262 mV) (Tab. 2) were found.

Temperature and time of incubation caused an increase in phosphate ions concentration which was the most pronounced at 5°C with systematically lowering Eh values (Fig. 4).
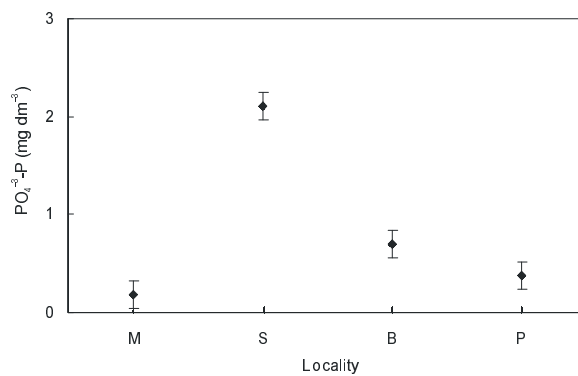
**Fig. 1**. Phosphate ions concentration in soil solutions of various localities of the Ciemięga river. Mean value ± standard deviation
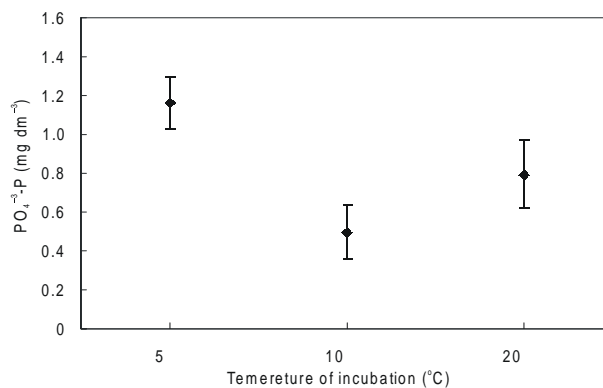


**Fig. 2.** Phosphate ions concentration in soil solutions of the Ciemięga at different temperatures. Mean value ± standard deviation
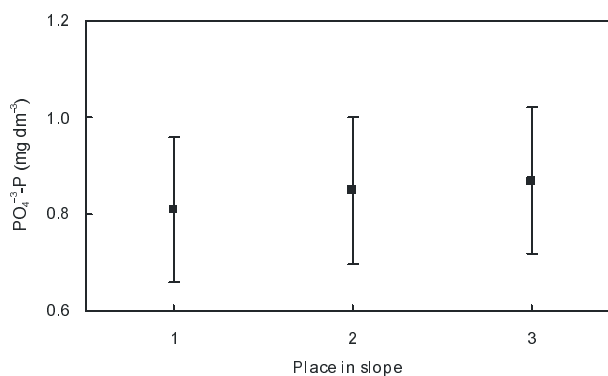


**Fig. 3.** Phosphate ions concentration in soil solutions of various places on slopes of the Ciemięga Mean value ± standard deviation
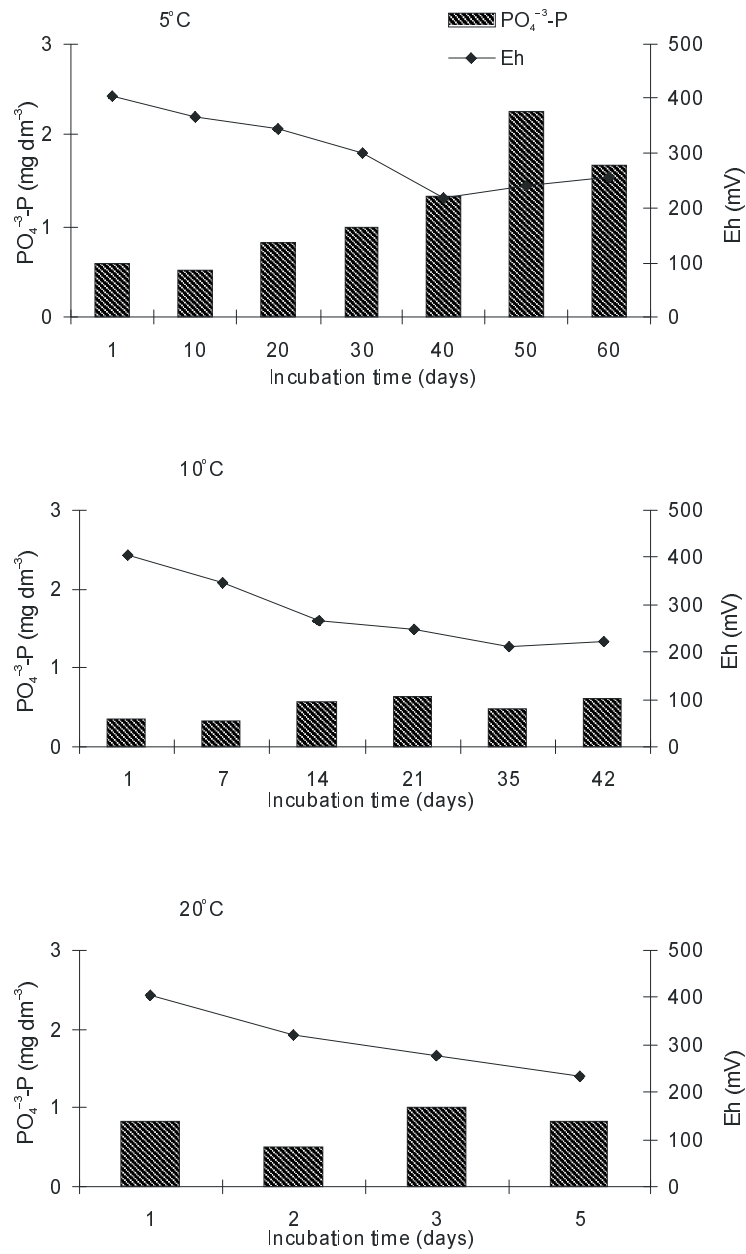
**Fig. 4.** Phosphate ions concentration and Eh (redox potential) changes during incubation of all soil samples from the Ciemięga catchment at different temperatures

## CONCLUSIONS

Analytical data obtained allowed us to show tendencies for directed changes of phosphate ions concentration in loess soils of eroded areas, caused by the excess of water and variation in temperature and also by differentiation in soil cover.

1. Phosphate ions $PO_4^{-3}$ concentration was in the range of 0.18-2.10 mg $dm^{-3}$.

2. The variations in concentration are caused by changes in soil cover due to erosion processes of soils, as well as to the temperature and time of soil samples incubation with currently lowering Eh values.

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# WYSTĘPOWANIE JONÓW FOSFORANOWYCH
## W GLEBACH LESSOWYCH

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Streszczenie. W doświadczeniu modelowym badano wpływ zalania gleb wodą (anaerobiozy) i inkubacji w zróżnicowanych temperaturach 5, 10 i 20$^o$C w czasie 0-60 dni na stężenie jonów fosforanowych w roztworze glebowym oraz Eh i pH w osadzie glebowym. Przebadano 12 próbek reprezentujących próchniczną warstwę wierzchnią gleb lessowych pobranych z różnych miejsc zlewni rzeki Ciemięgi k. Lublina. Stwierdzone stężenie jonów fosforanowych w granicach 0,18-2,10 mg· dm$^{-3}$ było zależne od miejsca pobrania próbek z gleb wzdłuż zlewni i z erodowanych zboczy, a także od temperatury i czasu trwania inkubacji.

Słowa kluczowe: jony fosforanowe, Eh, pH, gleby lessowe, warunki anaerobowe