

Letter to the Editor

Comment on: S. Nawara, T. Van Dael, R. Merckx, F. Amery, A. Elsen, W. Odeurs, H. Vandendriessche, S. McGrath, C. Roisin, C. Jouany, S. Pellerin, P. Denoroy, B. Eichler-Löbermann, G. Börjesson, P. Goos, W. Akkermans & E. Smolders. A comparison of soil tests for available phosphorus in long-term field experiments in Europe

Problem definition

In their recent study, Nawara *et al.* (2017) compared conventional, batch-extraction based soil P tests and the ‘diffusive gradients in thin films’ (DGT) technique for assessing the P requirement of European arable soils. The aim of their study was to compare various established soil P tests for their capacity to predict crop yield response to soil P, and to evaluate the relative importance of P quantity (Q) and intensity (I). The authors also derived upper limits of P deficiency (‘critical P values’) for each of the soil tests.

Regarding the current research focus on efficient fertilizer-P use in crop production, the efforts to close anthropogenic P cycles and reuse P-rich waste streams in fertilizer production, and the underlying limited global rock-phosphate reserves, this study is a valuable contribution towards a more accurate assessment of crop fertilizer demand in European soils. However, we noticed that the reported DGT values were obtained using different sampling times, depending on the quantity of CaCl₂-extractable P. The authors reduced the DGT sampling time to 2 hours for soils with large extractable P concentrations (P-CaCl₂ > 4.4 mg kg⁻¹) to avoid saturation of the DGT binding gel, and increased the sampling time for soils with small CaCl₂-extractable P (P-CaCl₂ < 0.8 mg kg⁻¹) to 48 hours to obtain measurements above the limit of detection. Soils with P-CaCl₂ between 0.8 and 4.4 mg kg⁻¹ were measured using the standard application time of 24 hours.

It is important to note that different sampling times affect the DGT measurement if P resupply to the sampler from soil is limited by P sorption to soil surfaces, which is typically the case. Therefore, the DGT dataset of Nawara *et al.* (2017) might contain artefacts. Different application times had also been used previously by Six *et al.* (2012) and Six *et al.* (2013), and we are concerned that this inconsistent implementation of DGT sampling might be repeated in future studies, especially by authors using the cited studies as guidelines for their own work. Moreover, we are concerned that the crop response models and derived upper limits of P deficiency presented in Nawara *et al.* (2017) will be used without critical

consideration of the experimental deficiencies of the underlying data. Below, therefore, we pinpoint the issue in the light of DGT theory applied to soil research, and we discuss the implications of varying the sampling time on the results and conclusions of Nawara *et al.* (2017).

Theory

Diffusive gradients in thin films is a passive sampling technique that was developed initially for sampling ionic solute species in water and sediments, but has since been applied to the assessment of solutes in soil pore water (Davison, 2016). During DGT sampling, anionic and cationic species diffuse through a hydrogel layer (‘diffusive gel’) and accumulate on a binding material (ion resin or metal oxyhydroxide) contained in a second, underlying hydrogel layer (‘binding gel’). Because of solute depletion in the vicinity of the DGT–soil interface, solute resupply from the soil solid phase is induced. In this way, DGT not only assesses the dissolved solute fraction and its replenishment by diffusion, but also measures the fraction that enters the soil solution by desorption and dissolution during sampling. The time-averaged solute concentration at the DGT–soil interface, C_{DGT} , can be calculated based on the exposure time, DGT geometry and mass of accumulated elements measured after elution or digestion of the binding gel (Davison, 2016).

The quantity of phosphate flux into the sampler is a function of the concentration gradient that is established, which in turn depends on the exterior (pore water) phosphate concentration and the thickness of the diffusive hydrogel layer. Depletion of the soil pore water phosphate concentration by the DGT sampler induces phosphate resupply from the solid phase by desorption. Because of the progressive depletion of labile soil P, the P flux into the sampler decreases during the DGT sampling period. Consequently, C_{DGT} also decreases continuously over time (Lehto, 2016). Although not studied in much detail, this effect has been demonstrated experimentally for P (Menzies *et al.*, 2005; Santner *et al.*, 2015; Menezes-Blackburn *et al.*, 2016). Figure 1, which is based on the data of Santner *et al.* (2015), shows C_{DGT} P values obtained for one soil with sampling periods of 4 to 192 hours. The C_{DGT} decreases progressively from 215 µg l⁻¹ (4 hours of sampling) to 64.5 µg l⁻¹ (192 hours of sampling). The 4-hour C_{DGT} value was 67% larger and the 48-hour C_{DGT} value was ~18% smaller than for the standard application time of 24 hours. Note that the 48-hour value in this dataset was estimated from the shape of the decreasing curve because there were no data available for this point in time. Figure 1 also shows that, for very short sampling times, C_{DGT} P was close to the pore water P concentration, and that it decreased to <50% at the 48-hour sampling and to <30% of the pore-water concentration for a sampling period of 192 hours.