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Geospatial modelling of soil phosphorus fractions and sorption indicators from heterogeneous landscapes in Ireland

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ABSTRACT

Soil mapping of phosphorus (P) pools at regional scale can be used to inform policy and land management strategies in agri-environmental systems. However, linking an element that is predominantly managed by fertiliser and organic inputs to regional scale geochemistry can be problematic. This study used a geological survey of the northern half of Ireland at ≤4 km^2 resolution to map total P (ICP *aqua regia*), plant available P (Morgan' P) and Labile P pools (ICP *aqua regia* and Mehlich-3 P). Spatial modelling was used to map P interactions with total and available aluminium (Al) (ICP *aqua regia* and Mehlich-3 Al), as predefined sorption indicators. With the aim to develop agri-environmental mapping approaches to link soil P sorption dynamics to geological controls that can assist with regional, catchment and national-scale modelling for policy development.

Plant available P concentration showed no spatial continuity in Kriged variogram output and was regulated by fertiliser inputs which mask any underlying geological processes. Subsequently, making this exploration method redundant in highly managed landscapes. Available Al concentrations determined by Mehlich-3 Al (M3-Al) are however regulated by underlying geology. Moreover, they have a significant negative correlation with bioavailable P indices. Areas of high M3 Al concentrations (≥ 702.5 mg kg^{-1}) are dominant in the study area and show mainly low plant available *P* values (<5 mg l^{-1}), however, potential labile P pools were indicated. Whereas areas of low Al concentrations (≤ 697 mg kg^{-1}) show moderate to high plant available P concentrations. Which could identify areas where P is likely to be more soluble and at greater risk to loss to water. Therefore, using available Al as a sorption indicator can identify regional areas of high P fixation and low soil P retention in soils. Furthermore, using sorption dynamics in geospatial modelling could benefit targeted management approaches.

1. Introduction

European Commission policies including the Water Framework Directive, Common Agricultural Policy and the Green Deal place a very strong emphasis on nutrient efficiency in agriculture and environmental protection across member states (MS). Programmes of measures (POM), designed and implemented at regional and national scale, need to account for the heterogeneous nature of soil and patterns in phosphorus (P) behaviour. Mapping P and its various forms is multifaceted as its concentration and bioavailability is attributed to pedogenic factors and chemical interactions as well as agricultural management and intensity (González Jiménez et al., 2018; Matos-Moreira et al., 2017; Mellander et al., 2016; Roberts et al., 2016, 2017; Smith et al., 2021). Due to the heterogeneous nature of soil across MS in Europe, there is a need for soil mapping approaches that can characterise and visualise P dynamics in order to better inform policy makers and agri-environmental advisors (Ballabio et al., 2019). As POMs are administered at farm and regional scale, policy on regulating P use is often derived from national scale maps (Micha et al., 2018, 2020).

The past two decades have seen an increase in the development of regional, national, continental and worldwide soil maps and databases, which has produced effective maps for soil chemical properties, resource assessment and soil and water quality protection (Arrouays et al., 2017; Ballabio et al., 2019). For nutrients such as P, global and European patterns of soil Total P (TP) stocks have been mapped and predicted by He et al. (2021) and Ballabio et al. (2019) for semi-natural and baseline concentrations over large areas. Fay et al. (2007), Geological Survey Ireland (2020), Viscarra Rossel et al. (2016), Panagos et al. (2022) and

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Rivero et al. (2007) have mapped TP stocks in Ireland, Australia, the United Kingdom and Florida (USA) using digital soil mapping approaches to aid policy formulation and land use management. It can also be beneficial if the development of agri-environmental measures and indicators is locally targeted based on identified environmental pressures and tailored to specific local conditions to help policymakers promote more sustainable agricultural methods (Fanelli, 2020; Neumann and Römheld, 2012). Digital soil mapping of plant available P has been carried out in France using high-resolution survey data to identify critical source areas at catchment scale but it would benefit from higher-resolution extractable Al data (Delmas et al., 2015; Matos-Moreira et al., 2017). In order to map P accurately and to understand its state and how it changes in the soil system, all chemical elements and environmental/chemical interactions in the soil system need to be explored.

Total P in soil can be divided into inorganic (P_i) and organic (P_o) forms, both of which are divided into labile and stable pools that are controlled by chemical interactions, fertiliser P inputs, crop removal and erosion/displacement (Delmas et al., 2015; González Jiménez et al., 2019a, 2019b; Graça et al., 2022; Kruse et al., 2015). Inorganic P in soil is often measured in agriculture and can generally be defined in three pools: (i) bioavailable to the plant (solution P), (ii) P held by the soil and likely to undergo a change of state to become available (labile P) or (iii) insoluble forms of P (non-labile P) (Khomenko et al., 2023; Menzies et al., 2005; Penn and Camberato, 2019). The soluble P pool is a function of P_i mineral fertiliser inputs, natural P_i from primary mineral weathering (e.g. apatite), desorption/adsorption of P from clay, aluminium (Al) calcium (Ca) and iron (Fe) oxides in the soil, and dissolution from secondary minerals that have an ability to bind P (Dunne et al., 2021a; Smith et al., 2021; Tawiah Croffie et al., 2022). The availability of P is also influenced by the P_o pool, in the form of plant residues and imported organic matter, such as manure/slurry, which in many cases contain non-labile P (Costa et al., 2016). The mobilisation of P_o is dependent on variables such as soil type, pH and the soil biota and redox potential (Graça et al., 2022).

Chemical extrications are used to measure the plant-available fraction in a soil sample and are calibrated against crop-yield fertiliser response in field trials (González Jiménez et al., 2018). Soils are assumed to have the same rate of response to P fertiliser input regardless of their sorption properties, although this is not always the case (Dunne et al., 2021a). Agronomic soil P testing is typically used to generate fertiliser recommendations and can be mapped to visualise available P at regional and national scales. The P transfer continuum (Haygarth et al., 2005) identifies STP as a P source in the conceptual model of P loss to waterbodies. Water quality research using catchment-scale models include STP, coupled with flow data, as an input variable to simulate P export from catchments. Using STP for P measurement and modelling in isolation to other soil attributes does not account for variation in relevant soil characteristics, such as P sorption and desorption properties, at regional, catchment and national scales (Dunne et al., 2021b). Previous studies have signalled that effective P management requires linking STP with other soil attributes that describe differences in soil P buffering capacity especially in a diverse landscape with contrasting soil parent materials (Daly et al., 2015; Dunne et al., 2020).

The heterogeneity of Ireland's landscape is a result of its geological history, including three successive glaciations, as well as geomorphology and climatic influences (Geological Survey Ireland, 2018). Broadly speaking, areas of higher ground tend to be found around the margins of the island and more southern areas, with the Midlands being flat or gently undulating. This largely corresponds to bedrock geology, with the Midlands dominated by Carboniferous limestones, whereas north and western areas are underlain by schists, Dalradian metasediments, and igneous rocks; the southwestern region by sandstones and mudstones; with greywackes and some igneous rocks in the east (Geological Survey Ireland, 2022). All are variably overlain by Quaternary deposits, which further influence the landscape and soils. Furthermore, a variable meteoric parameter which implicates heterogeneous soil formation, is precipitation. In Ireland the western coastal areas have the highest annual rainfall, which coincide with ombotrophic (rain fed) peats, whereas the southeast tends to have the lowest rainfall averages (Schulte et al., 2018). Combining these influences, and for the purpose of relating geochemistry to P bioavailability, this translates to: high Al and Fe hydrous oxide concentrations in the north and eastern regions; higher Ca concentrations and lower Fe/Al content in the midlands/southern region; and high organic content soils in the west (i.e. Peat and Peaty mineral soils), which have a lower P adsorption capacity (González Jiménez et al., 2019a, 2019b, Geological Survey Ireland, 2022, Fay et al., 2007).

Several soil extractions are used for the determination of plant available-P for critical soil index systems (Vero et al., 2022). For example, but not limited to; Olsen P, Mehlich-3 P, Morgan's P, Bray's P, oxalate-extractable P. All which evaluate different P pools and target a particular soil type (Neyroud and Lischer, 2003; Vero et al., 2022). As a result, extractable P concentration differs in all STP's (Neyroud and Lischer, 2003). Therefore, STP is calibrated against crop yield (Schulte and Herlihy, 2007). One STP that provides insight to P sorption behaviour, and had been calibrated against yields in Irish soils, is the Mehlich-3 (M3) extractant. This extract is used to determine labile/Al bound and easily available/labile P (M3-P) and aluminium (M3-Al) from the same extract (Daly et al., 2015; Schulte and Herlihy, 2007). Dunne et al. (2020) categorised M3-Al as a separator/driver of two different sorption behaviours in Irish soils: (i) a low concentration range of M3-Al (<697 mg kg^{-1}), which displays a gradual decrease in sorption to the soil particles as P increases, and (ii) a high concentration range of M3-Al (>702.5 mg Kg^{-1}) where there is rapid P sorption to the soil particles and a low final plant-available P concentration. Dunne et al. (2020) proposed that including sorptive behaviours in P management can lend itself to soil type-specific P advice for agriculture. For example, soil with low sorption capacity will accumulate applied P in a more soluble form with potentially greater loss to runoff compared to high Al soils. High-Al soil has a rapid P-sorption capability and will thus have a tendency to 'fix' applied P to soil P reserves, leading to a higher risk of ineffective or inefficient fertiliser use. Such soil requires tailored P management (Dunne et al., 2020; Dunne et al., 2021a).

The objective of this study was to map P bioavailability and P sorption indicators at regional scale to aid future decision making on soil health and management in Ireland. An existing archive of soil samples and accompanying database from the Tellus programme were used to determine available P, sorbed/precipitated P which has potential to be desorbed/dissolved into solution, and Al in topsoil samples (5–20 cm), collected across a 35,716 Km^2 heterogeneous landscape in Ireland.

2. Methods

Geological Survey Ireland's Tellus programme has completed a soil survey of the top half of the country, collecting c. 10,000 topsoil samples (https://www.gsi.ie/en-ie/programmes-and-projects/tellus/Pages/default.aspx). In the present study, all available samples in the topsoil archive were analysed to determine P pools identified in Fig. 1, using both Morgan's and M3 solutions as extractants, with the aim of visualising the geochemical spatial distribution of Morgan's P and M3-P at regional scales and developing agri-environmental indicators of P behaviour in soil. Including extractable-Al together with the Al cut-off points (developed by Dunne et al., 2021a) provides an indicator of P sorption mechanisms (see Fig. 1 for methodology flow chart).

2.1. *Terra soil survey*

Soil samples (5–20 cm) have been collected by the Tellus programme in Geological Survey Ireland since 2011, from a total of 9921 sites in the northern half of Ireland. Sample collection of the southern half of the dataset is ongoing. Sample location was predefined based on a schematic survey design of fishnet of even-numbered easting and northing lines on

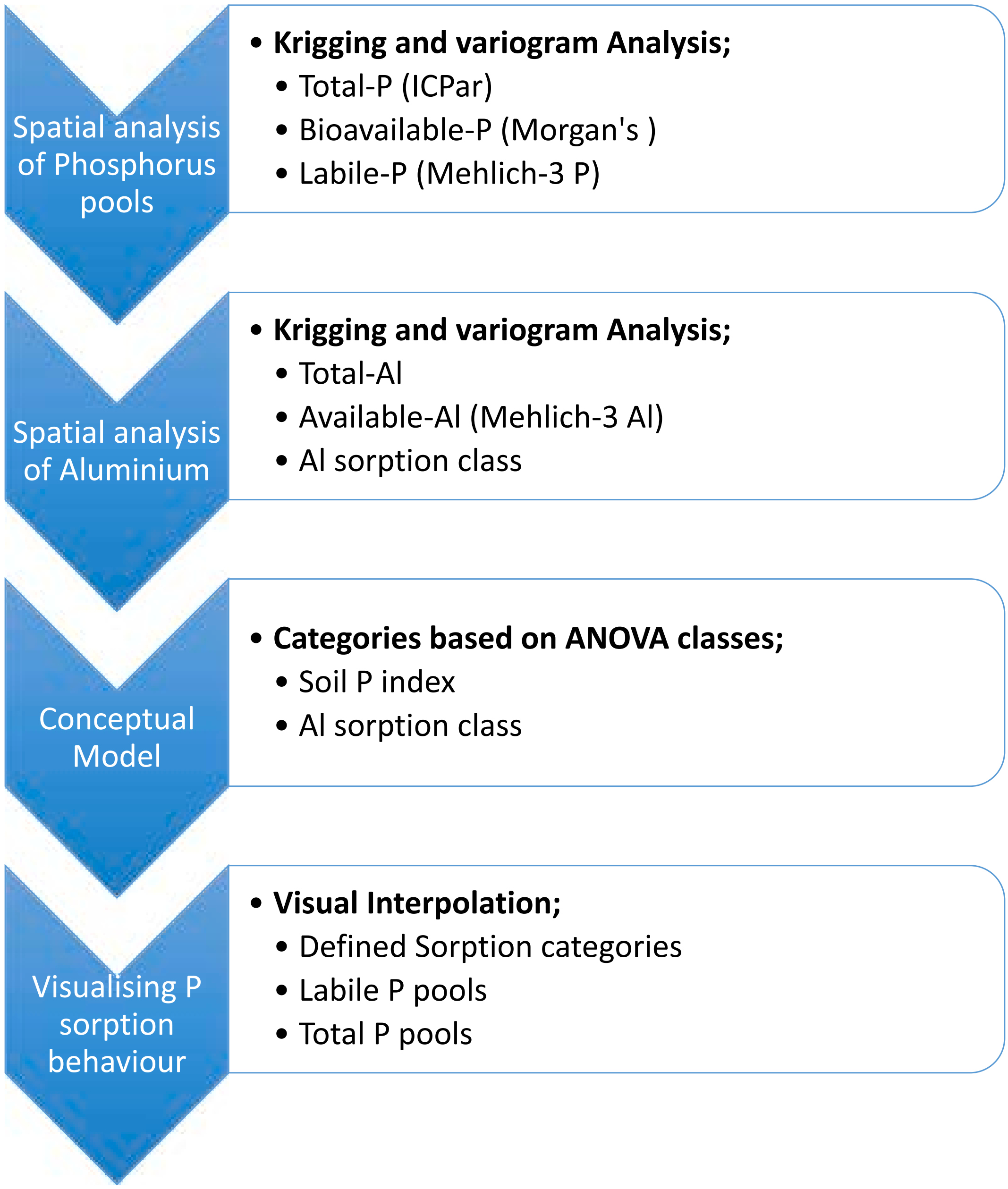

Fig. 1. Methodology Work Flow.

the Irish National Grid (Geographic Coordinate System: GCS_TM65). The survey design aimed to collect a variety of geological domains in Ireland. Samples were collected at a typical density of one sample per 2 × 2 kilometres (4 km^2) in rural areas and at a density of one sample per square kilometre (1 km^2) in the Peri-urban areas of Dublin and Galway (Geological Survey Ireland, 2020). Five composite samples were collected per field within a 20m^2 square grid. With the first point in the middle of the square, and remaining four points 10 m from the centre in a north, east, south, west direction. Further details of the survey methods are contained in Geological Survey Ireland (2020).

2.2. Soil analysis

Samples were prepared and analysed as part of the Tellus programme (Geological Survey Ireland, 2020). All samples were dried at 30 °C, disaggregated and sieved to 2 mm. Organic Matter percent (OM) by Loss-on-ignition analysis and pH by calcium chloride ($CaCl_2$) slurry method. Samples were milled to <32 μm prior to analysis by inductively coupled plasma mass spectrometry (ICP-MS) following extraction by *aqua regia* (conc. HCl:HNO_3 in ratio 3:1) (ICPar). ICPar-P and ICPar-Al are used as a measure of 'Total' concentrations. It should be noted that many mineral phases, including the important framework silicates, are not readily dissolved by *aqua regia,* however, for the purpose of this work and consistent with previous agronomic studies, the Tellus ICP-ar data was used as proxies for total Al and P (see supporting information) (Fay et al., 2007).

Morgan's P was extracted from soil samples (6.5 ml) using 0.5 M sodium acetate acetic acid, in a soil:solution ratio of 1:5 *v*/v and analysed colorimetrically with the molybdate blue method using a LACHAT analyser (Daly et al., 2015). M3 soil extracts were obtained using a 1:10 soil:solution ratio, with 2 g of soil shaken with 20 ml M3 reagent (0.2 m CH_3COOH + 0.25 m NH_4NO_3 + 0.015 m NH_4F + 0.13 m HNO_3 + 0.001 m EDTA) for 5 min on a reciprocating shaker (Daly et al., 2015). M3 extracts were then filtered (using 0.45 μm filter paper) and analysed by inductively coupled plasma – optical emission spectroscopy (ICP-OES) to determine labile forms of P and Al.

2.2.1. Soil P pools

Bioavailable-P in Ireland is measured and calibrated against crop yield to incorporate management advice by Morgan's P. Therefore in this study Morgan's P is an indirect measurement of plant available-P (mg l^{-1}).

Labile P is the fraction which can undergo a change of state to become available to the plant under optimum conditions. In this study M3 (mg Kg^{-1}) is used as a measurement of easily-available labile P pool. The M3 reagent contains ammonium fluoride which enhances the release of Al and Fe phosphates, and suppresses adsorption from P colloids. Furthermore, nitric acid addition of the reagent aids dissolution of available P from Ca and Fe bound P (Song and Ketterings, 2010).

Morgan's P was reported as nutrient weight per sample volume (mg l^{-1}) and M3 was reported as nutrient weight per sample weight (mg Kg^{-1}). As the soil P tests are were designed to report different units, figures which show P concentration distribution were classified by their representative soil P index (Table 1).

2.3. Soil P index and Al cut off

Morgan's extract is used to determine available P for agronomic applications and values are placed in bands or indices to provide fertiliser advice in productive agricultural systems (Table 1). In this study, Morgan's *P* values determined on the Tellus topsoil archive samples were placed into P indices to identify soils that are (a) deficient and low in available P (index 1&2), requiring build-up with fertiliser application; (b) at the target value of available P level (index 3) or (c) have excess available P and require a drawdown of P to reduce the environmental risk to local watercourses (index 4). Mineral soil samples were separated from organic soil samples in this dataset. Soil samples with an OM content above 20% are classed as organic-rich soil or peat, and were not analysed for Morgan's P with accordance with Irish soil testing guidelines (Wall and Plunkett, 2021; González Jiménez et al., 2018). Such soil is automatically assigned to soil P Index 3 and must to be managed for 'maintenance rates' only (Wall and Plunkett, 2021, González Jiménez et al., 2018). In maps produced for this study we have assigned the organic/peat soil samples an index 0 to separate them from mineral soil samples assigned to soil P Index 3.

There is no Irish soil P Index for M3-P so the New York State index system (Ketterings et al., 2001) has been adopted for this study and is used in maps presented here. The New York State system has five classes: very low, low, moderate, high and very high (Table 1).

Previous studies on Irish soils (Dunne et al., 2021a) used hierarchical clustering to identify a separation of P sorption behaviour influenced by two ranges of M3-Al. A low range of M3-Al (2.5-697 mg kg^{-1}) was associated with slower rates of P sorption, and higher range of M3-Al (702.5–2460.8 mg kg^{-1}) associated with rapid sorption of P. Therefore, soil samples were further classified as Low Al ($<$ 697 mg kg^{-1} M3-Al) or high Al ($>$ 702.5 mg kg^{-1} M3-Al) based on the cut off classification of Al sorption potential proposed by Dunne et al. (2020).

2.4. Mapping of soil P and Al

GSI's Tellus Programme has to date carried out digital mapping of its soil geochemical Terra Soil data in ArcGIS using various methods, including simple dot maps and continuous surface maps. For the latter, it has employed Inverse Distance Weighting (IDW), an interpolation method that assumes that samples closer together have characteristics more alike than those further apart. This assumption is reasonable for neighbouring geochemical soil samples derived from similar bedrock source material. GSI has typically employed IDW using a search radius of 2000 or 2500 m (e.g. GSI, 2020). For the 2 $\times$ 2 km grid employed for sampling this generates an interpolated surface that closely reflects the measured values of the data points. IDW has thus been employed for mapping the data for this project.

Mehlich-3 and Morgan's P data are measures of the plant available fraction in soil samples. As such the assumptions that underpin mapping of Tellus soil geochemical data may not necessarily hold for Terra Soil. This is particularly the case for elements such as P, for which sources such as agriculture may give rise to a less coherent spatial distribution of the element, i.e. one that does not reflect underlying bedrock control (Young et al., 2016).

In order to assess the degree of spatial coherence in the Morgan P and M3-P data, kriging and variogram analysis was carried out. Kriging is another interpolation method that is similar to IDW but also provides an estimate of the error or uncertainty in the predicted interpolated surface. As such it can provide useful insights into how well the data are correlated spatially and thus how best to interpret the interpolated maps. A work flow diagram has been provided in Fig. 1 of spatial analysis.

Kriging was conducted using the following parameters: grid cell size of 1000 m, variogram width: 1000 m, variogram cut-off distance: 50000 m and kriging search distance: 2500 m. Variograms were generated using the R package *automap* and the function *autofitvariogram*. Semi-variograms were generated as isotropic (no bias in direction) and kriging was carried out using the R package *gstat*. The data have been evaluated in two ways: (i) variography/kriging with no screening/filtering of the data, and (ii) variography/kriging based on data below the 95th percentile.

The variogram map analysis is categorised into isotropic or anisotropic geospatial continuity shown by variogram maps. Isotropic geospatial continuity means that there is a broad regional signal which is statistically viable and does not show variability between sample points and can be used in interpolation. Variogram maps with anisotropic geospatial continuity show a very short distance between sample sites where there is similarity in the element signal with variability between pairs of points at various distances and therefore not recommended for interpolation. Fig. 1 shows a work flow chart of the process of visualising spatial dynamics of soil P.

3. Results

3.1. Mapping soil P fractions and soil P index

Kriged maps of the distribution of P analysed by the three different methods (Total P, plant available P and labile P; ICPar, Morgan's and M3, respectively) display considerable differences (Fig. 2). The ICPar-P data display broadly coherent patterns that reflect underlying soil characteristics, notably the proportion of OM in peatland/organic soils (peat maps can be found in supplementary information). Thus, areas of blanket bog such as in the west and northwest, as well as of raised bogs in the midlands, have very low ICPar-P concentrations ($\leq$500 mg kg^{-1} as recorded by Fay et al., 2007). The lower values observed mainly consisted of soils in peatland regions with a sandy A horizon. Mineral soils generally have much higher ICPar-P concentrations, with those overlying in the northeast of the mapped area and these Dalradian rocks having particularly high values ($>$72 mg kg^{-1}, Fig. 2). This may reflect a mixture of influences, including bedrock itself and anthropogenic inputs to soil used as both pasture and arable land (shown in supplementary information).

The variogram for ICPar-P data shows a broad near-isotropic geospatial continuity. The kriged map of Morgan's P data is characterized by a general lack of spatial coherence, with high and low values dotted across the map to give a "spotty" appearance. Some of the areas of blanket bog, notably in the north east and east midlands, have relatively high Morgan's *P* values ($>$7.87 mg l^{-1}), and apparently reflecting higher solubility of P in soils with high OM content ($>$20%) (González Jiménez et al., 2019a, 2019b; Roberts et al., 2017). The variogram for Morgan's P data shows a lack of covariance structure and short range of geospatial continuity. The map of M3-P displays a distribution that falls somewhere between that for ICPar P and Morgan's P, with similarly high values in the northeast of the survey area and in east Donegal mirroring those of ICPar P, while high values in some areas of blanket bog invite

Table 1
Soil P index system based on Morgan's P and Mehlich-3 P extractions.

Soil P Index	Index Description	Response to Fertilisers	Soil P Ranges (mg/l)	
			Grassland crops	Other crops
Morgan's P				
1	Very Low	Definite	0.0–3.0	0.0–3.0
2	Low	Likely	3.1–5.0	3.1–6.0
3	Medium	Unlikely/Tenuous	5.1–8.0	6.1–10
4	Sufficient/ Excess	None	Above 8.0	Above 10.0
M3-P Soil P (mg/Kg)				
1	Very Low	Definite	1–12	
2	Low	Likely	13–22	
3	Medium	Unlikely/Tenuous	23–35	
4	High	None	36–68	
5	Very High	None	69 +	

comparison with Morgan's P data. The variogram for M3-P data indicates a significantly greater degree of spatial coherence compared to the Morgan's P data.

Morgan's P values determined for this study were assigned a Soil P index (Table 1, Fig. 2d), with 29%, 31%, 19% and 20% of samples classified as P Index 1, P Index 2, P Index 3 and P Index 4, respectively. Soil P Index 4 comprised of Morgan's P values ranging from 8 to 209 mg l^{-1}. These samples do not include those with measured LOI (OM) > 20%, which comprise 38% of all samples collected in the study area. These samples are classed as organic-rich soil or peat. Such soil is not included in the P Index system which is confined to mineral soils. Soil P index when mapped (for mineral soils) shows a broad near-isotropic geospatial continuity which shows more value in spatial coherence.

3.2. Mapping total and available Al

Maps of both Al analysed by ICPar and M3 (Fig. 3) display strong coherence between higher Al (14,678 and 847 mg kg^{-1} for ICPar and M3-Al respectively), and bedrock or till dominated by clastic rocks, such as the Dalradian rocks of the north east and the Lower Palaeozoic rocks of Longford-Down. Areas of low Al typically reflect topsoil with high OM content (>20% in this study), such as blanket bog in the west and northwest and raised bog in the midlands. Variogram analysis shows a spatially coherent covariance structure (Fig. 3).

Mineral soil M3-Al values were categorised into high/low classes with 41% of samples having low M3-Al (<697 mg kg^{-1}) and 59% high M3-Al, respectively (Table 2).

3.3. Mehlich-3 Al influence on soil P index

Concentrations of M3-Al in soil samples in the survey area ranged from 0.02 to 2671 mg kg^{-1} with a mean and median of 620 and 663 mg kg^{-1}, respectively. M3-Al values were compared to the P Index for mineral soils (Fig. 4) and a direct relationship was found (one way

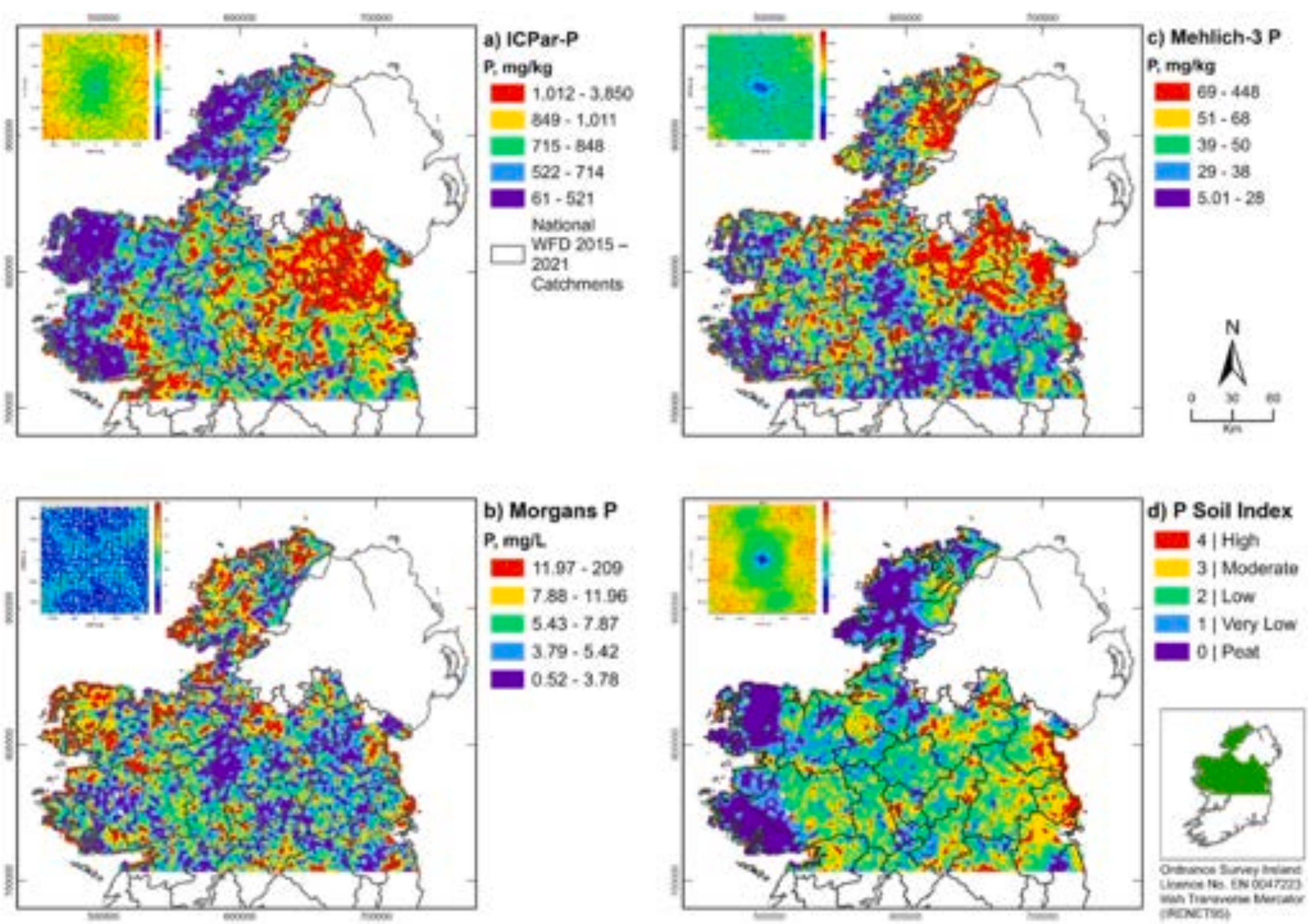

Fig. 2. Kriged maps of a.) Total P, c.) Morgan's P c.) Mehlich-3 P and 4.) Soil P Index (colour). Morgan's P displayed in colour bands of the Irish soil index system, with >12 mg l^{-1} as P saturated (Dunne et al., 2021a). Mehlich-3 P colour bands as Soil index system described as Ketterings et al. (2001). Data smoothing was used to build this data model, therefore, this map is not to be used as an exact concentration for the location it is presenting.

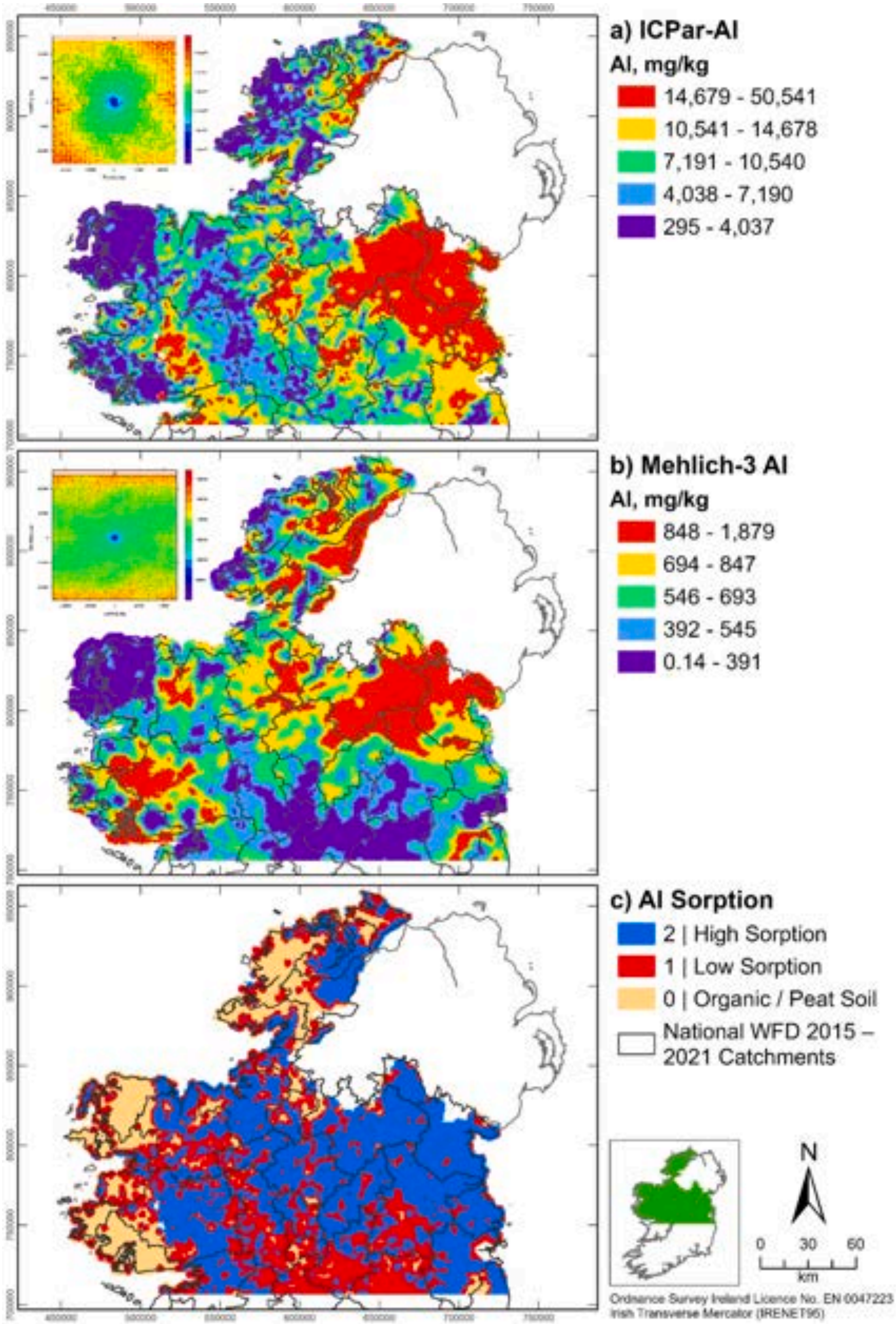

Fig. 3. Kriged maps of a.) Total Al, b.) Mehlich-3 Al, c.) Al Sorption classifications..

Table 2
Summary of soil P Index categories in Al cut off categories.

Soil P Index	Low Al		High Al	
	Count	%	Count	%
1 – Very Low	486	14	1353	39
2 - Low	755	22	1156	33
3 – Moderate	581	17	610	17
4- High	840	24	376	11

ANOVA, with Tukey Pairwise analysis, Fig. 4, Table 3). There was a significant difference between low-P status soils (soil P index 1 and 2), moderate and high-P status soils in ANOVA comparison analysis and interval plots (F value = 218, *p* value = 0.000). Fig. 4a shows the negative distribution extractable M3-Al concentration has on the soil P index in mineral soils. A line has been placed on Fig. 4a to visually distinguish the M3-Al sorption categories. Moderate and High P status soils (C and D from Turkey Pairwise Analysis) which are in the Low M3-Al sorption category have been mapped in Fig. 5 and Low P status soils (A and B from Turkey Pairwise Analysis) which are in the High M3-Al sorption category have been mapped in Fig. 6.

4. Discussion

4.1. Geospatial distribution and interpolation of phosphorus pools

4.1.1. Total phosphorus (ICPar-P) kriging and variogram analysis

As shown in Fig. 2, high soil ICPar-P concentrations, as measured for the Tellus programme, (>850 mg kg^{-1}) are observed mainly in eastern regions, consistent with previous Irish survey results (Fay et al., 2007, Mcgrath and Fleming, 2007). These areas comprise with a high proportion of land classified as pasture and arable land (e.g. north Co. Dublin) (Corine land use data, see SI). They are also notable for high stocking rates of cattle (see SI).

Soil P mainly originates from weathering of bedrock minerals (Walker and Syers, 1976). The highest ICPar-P soil contents have been recorded in areas where bedrock is dominated by clastic rocks (north east midlands, North East), indicating a broad coherence between bedrock type and ICPar-P content of soil. However, within these areas the distribution of ICPar-P is irregular, with no detailed bedrock control,

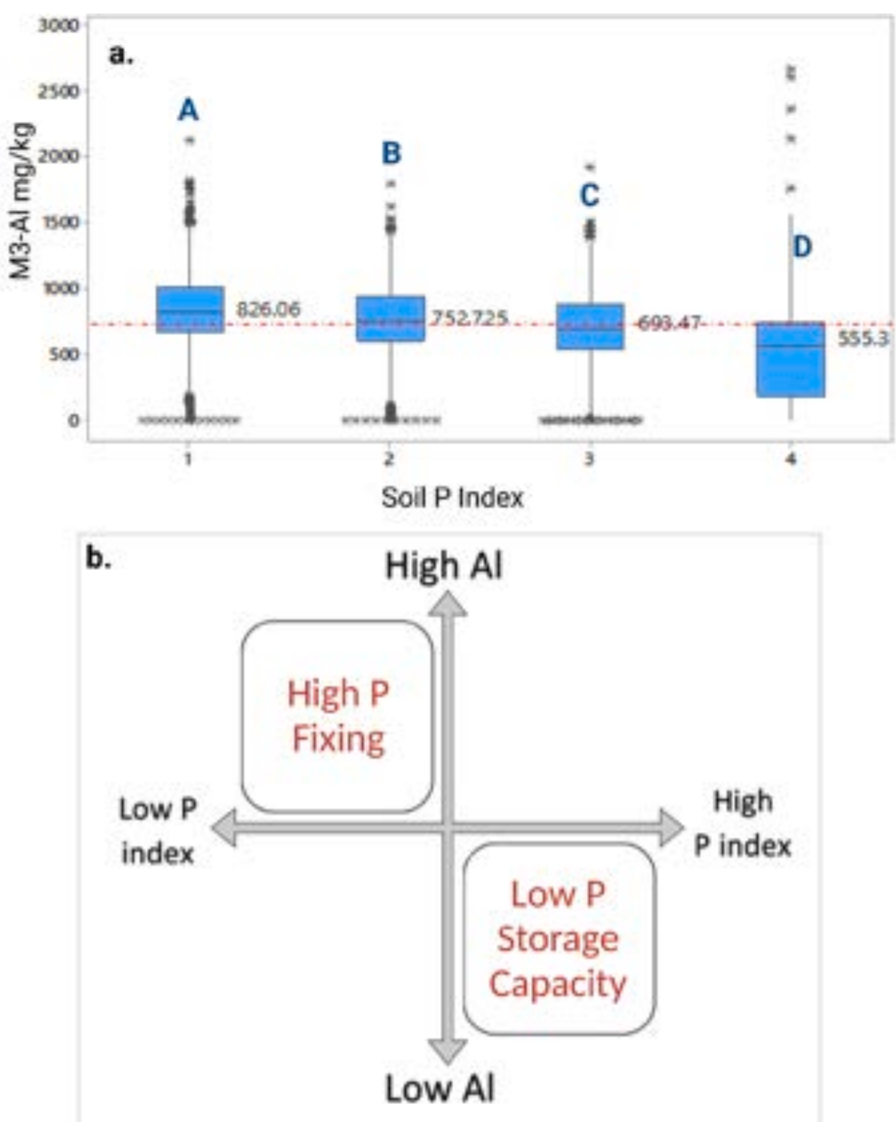

Fig. 4. Extractable Al (Mehlich-3 Al) concentrations grouped by soil P Index with sorption index cut off point, a.) Box plot of M3-Al concentration in soil P Index category with ANOVA Tukey Pairwise groupings (A, B, C, D), b.) Low P storage capacity '*low P sorption soils*', and High P storage and P fixing capacity '*High P fixing soils*' soil categories identified as needing specialist management strategies to meet the target soil P index.

Table 3
ANOVA Analysis.

	DF	Adjusted Sum of Squares	Adjusted Mean Squares	F-Value	*P*-value
Soil P Index	3	60,403,479	20,134,493	218	0.000
Error	6011	556,226,871	92,535		
Total	6014	616,630,350			

a possible consequence of anthropogenic factors, including agricultural inputs. The study area is dominated by managed agricultural land (70%). In such concentrated areas of land management addition of P fertilisers may confound any underlying patterns of P distribution that reflect bedrock control and give rise to poor spatial coherence of ICPar-P. Therefore, any isotropic geospatial continuity in the East Midlands will be mainly agricultural inputs.

4.1.2. Plant available and labile phosphorus kriging and variogram interpolation

In contrast to ICPar-P, variogram analysis of Morgan's P data (Fig. 2) showed no spatially coherent covariance structure and discrete anisotropic patterns. Variogram analysis of M3-P data suggested greater spatial coherence than for Morgan's P, but mainly with significant anisotropy in the eastern region where there is a high proportion of land classified as pasture and arable land (see SI). Therefore, in some regions (i.e. East Midlands) there is geospatial continuity in M3 which can be used in interpolation. However, the lack of strong geo-statistical correlation among samples for plant available P/labile P indicate that interpolation of the data is unlikely to produce reliable predictions of soil concentrations for areas between sample points for the whole sampling area.

4.1.3. Soil phosphorus index kriging and variogram interpolation

A map generated by interpolation of the P Index by kriging (Fig. 2d) shows hotspots of high P index and large areas of low P index (Index 1 and 2). Mapping Soil P Index shows near-isotropic geospatial continuity compared to Morgan's P concentration, and in turn, showed significant regional trends in the data. This provides a more statistically viable approach to visualising available P than by semi-variogram analysis (by Morgan's P), yet, this mainly reflects the geogenic foundation of Peat soils. Moreover, peat and organic-rich soils have been assigned their own class in this study and do not provide information on plant available P in the soil system.

High application or 'build-up' rates of P are not advised on peat and organic-rich soils as they have no capacity for P storage. Therefore, it is unsurprising that these large areas of blanket bog shown in SI are creating directional bias in variogram output. Additionally, as P concentration can change from fertiliser addition, visualising soil P Index at this scale only showed P concentration groupings from temporal anthropogenic sources and not necessarily P sorption behaviour by soil type or geochemistry.

4.2. Relationship between Al and soil P index

In Fig. 3 areas of lowest Al coincide with areas of peat (Fig. 3a and b). This is in line with previous survey data in Ireland (Fay et al., 2007, McGrath and Fleming, 2007). The spatial distribution of areas of high ICPar-Al and M3-Al shows strong coherence with the distribution of clastic rocks, notably the Dalradian metasedimentary rocks of the north east, the Lower Palaeozoic greywacke in the east midlands, and basal Carboniferous sandstone and shale in the midlands. Even in midland areas of dominant limestone bedrock the Al content of mineral soil is still relatively high (Fig. 3).

Data plotted in Fig. 4 in this study, indicated that soils in P indices 3 & 4 were more likely to have low M3-Al, and soils with soil P Indices 1 & 2 are more likely to have high M3-Al values. Other P sorption parameters have been linked with M3-Al. For example, Daly et al. (2015) identified a break-point at M3-Al equal to 615 mg kg^{-1} to describe the relationship between P buffer capacity and M3-Al using a broken-line regression in a subset of Irish mineral soils. Similar work has been described by Dunne et al. (2021a,b). However, this is the first large-scale survey that has demonstrated a direct link between soil P index and M3-Al concentration.

In comparing soil P index and M3-Al only mineral soil samples have been used as peat and organic-rich soils are generally acidic with low clay mineral and Al/Fe oxide contents, which result in poor P sorption and P reserves (Daly et al., 2001; González Jiménez et al., 2019a, 2019b; Roberts et al., 2017). Soils classified as organic-rich or peat (OM > 20%) are characterized by levels of OM that occlude P sorption to silt and clay particles. When P is applied to these soils, it remains in the solution phase (Daly et al., 2001), posing a risk of loss to water in hydrologically active areas. As a result of this P behaviour, agricultural advice limits P application on these soils to allow only 'maintenance rates' of fertiliser P to replace P removed in crop offtakes (Roberts et al., 2017). Operationally, for nutrient management at farm scale, soils that fall into this organic-rich/peat category are not analysed for Morgan's P but their P content is maintained (Wall and Plunkett, 2021). As these soils have their own management framework only mineral soils will be included in the discussion of soil P indices and M3-Al.

4.3. Visualising the influence of M3-Al on phosphorus sorption in soil

Soil management systems require that high P status soils are in need of P concentration 'draw down' through primary production (Dunne et al., 2021a, 2021b). Similarly, P deficient soils require 'build-up' of P before it will become available to the plant (Daly et al., 2015). However, this relationship is not linear and soil type will dictate the efficiency of 'draw down' and 'build-up' phases, which is not captured in the index systems (Dunne et al., 2021a). Moreover, high available Al, such as M3-Al in soil, will have a confounding effect on P sorption behaviour (Delmas et al., 2015; Matos-Moreira et al., 2017). As identified in Fig. 4a, each soil P index has a significantly different M3-Al concentration grouping, and when coupled with high and low sorption categories, two groups of P behaviour are identified (Fig. 4, Low P storage capacity '*low P sorption soils*' are described by high soil P and low Al, and High P storage and P fixing capacity '*High P fixing soils*' described as P deficient soils with high Al). These soil categories will need specialist management strategies to meet the target soil P index.

4.3.1. Visualising low P sorption soils

Low P Sorption (high P Index, low Al) soils may have limited capacity to store additional P, causing a potential threat to water quality. In the survey area, Low P Sorption soils (high P, low M3-Al) mainly occur across the southern part areas and in coastal regions (Fig. 5a). The WFD catchments surrounding the east (Nanny-Devlin to the north and Liffey and Dublin Bay to the south, see Fig. 5b) contain extensive areas of high P and low M3-Al soil, covering c.50% of the catchment. In the Nanny-Devlin catchment 31 of 34 rivers have a poor water quality status (EPA, 2019). Furthermore, the Liffey and Dublin Bay catchment comprises nutrient-sensitive areas considered to be at high risk from diffuse pollution (Peñalver et al., 2021).

These soils will need to be carefully managed to avoid further risk to local marine and fresh water quality, especially soils above the 8 mg l^{-1} threshold. Additionally, low P sorption soils are surrounded by soils with higher concentrations of organic matter (>20%, see supporting information for peat maps). Europe's agri-food policy aims to ensure food security in the face of climate change and biodiversity loss, and the Soil Health Monitoring Law proposal has an emphasis on management to, increase carbon storage and mitigate against CO_2 emissions. This has a direct impact on soil P management as organic matter competed for sorption sites, reducing the soils ability to sorb P (González Jiménez

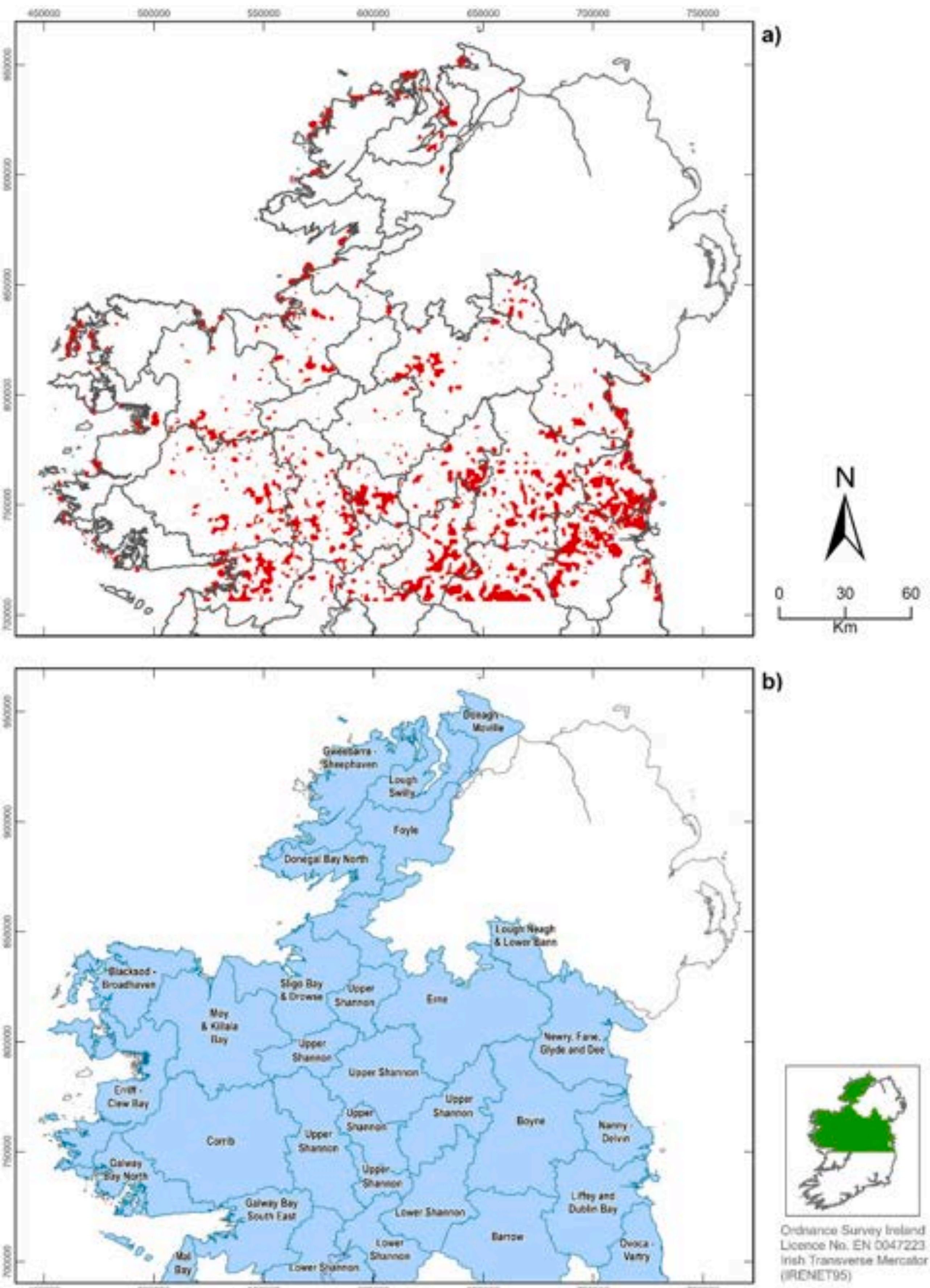

Fig. 5. a.) Map of Low P sorption areas (Moderate to high P and Low Mehlich-3 Al), b.) Catchment names.

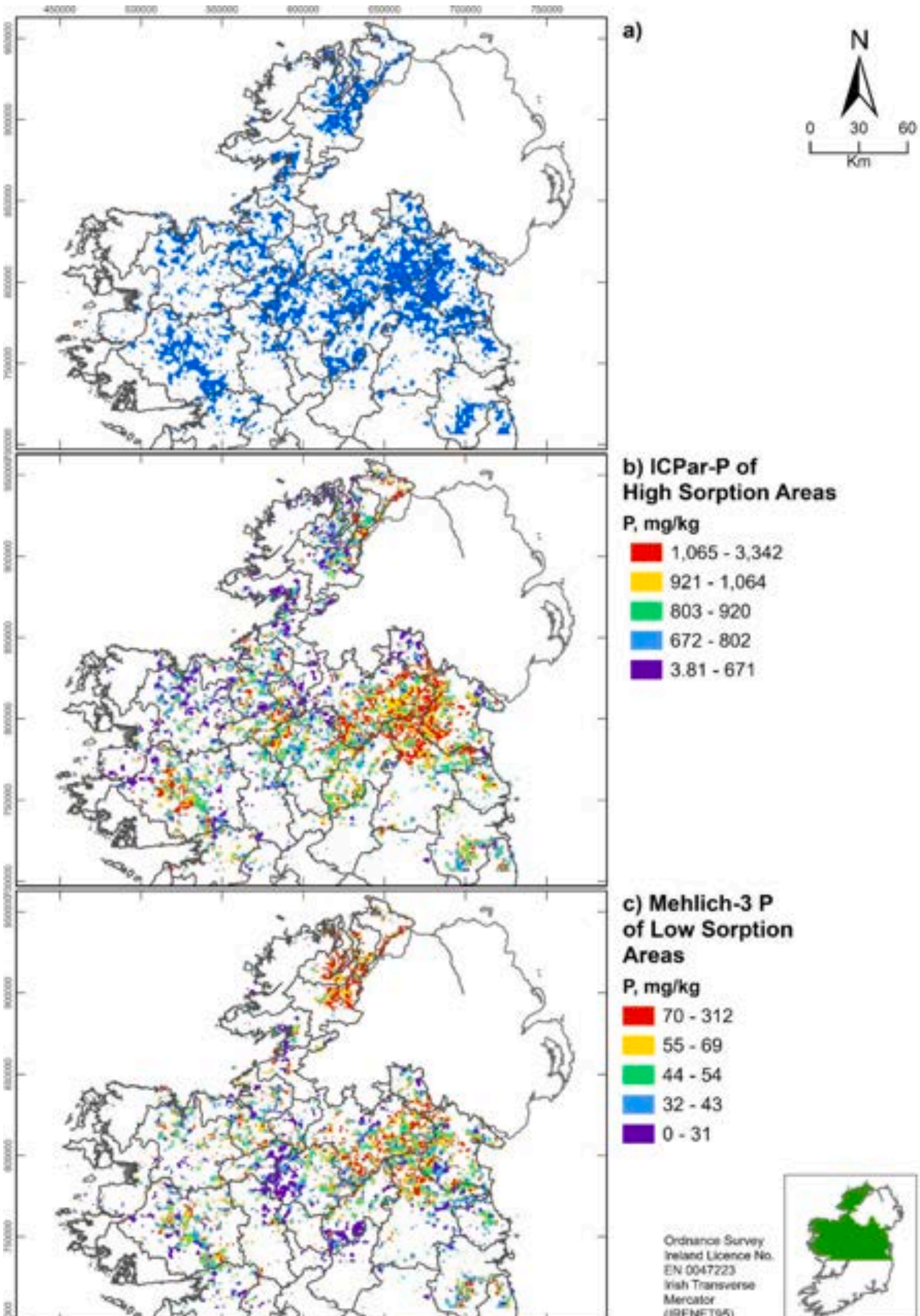

Fig. 6. High P sorption areas; a.) High Al and Low soil P index, b.) High Al and Total P concentration, c.) High Al and Mehlich-3 P concentration . IDW was used to produce this map. As IDW uses smoothing to present the data, this map is not to be used as an exact concentration for the location it is presenting.

et al., 2019a, 2019b). Therefore, careful management of these soils is needed to minimise the possibility of P exports to receiving waters when organic matter is increased (González Jiménez et al., 2019). Maps of P Indices classified in this way have the potential to assist land managers/government/advisors to plan for WFD targets to achieve good water quality status in these catchments (Daly et al., 2015; Dunne et al., 2021a). However, as the data in this category was "spotty", it is recommended that the survey is completed at national level to get a more coherent picture of Irish soils with low P sorption.

4.3.2. Visualising high P fixing soils

High fixing soils (low P/High M3-Al) may be slow to build-up available P. As noted, P-deficient soils require the accumulation of P in labile pools before it becomes available to the plant. Otherwise, available P pools may decline/fail to develop when simultaneously utilised by the plant (Daly et al., 2015). These soils will need careful management to build-up soil P pools and may not need to adhere to ideal spreading conditions as they are likely to retain P (Dunne et al., 2021a).

High P-fixing mineral soils identified in Fig. 6a were mapped together with the WFD catchment boundaries (see Fig. 2c for explanation of catchment boundaries). High P-fixing soil (low P/high M3-Al) occurs over a significant part of the survey area, which is where bedrock comprising clastic and metasedimentary rocks rich in aluminosilicate minerals is dominant. However, in these areas of low Morgan's P, i.e. where the P Index is 1 or 2, both the Labile P and Total P (M3- P and ICPar-P) concentrations are generally relatively high (54 and 920 mg Kg^{-1} for M3-P and ICPar-P, respectively. Fig. 6b and c).

Variogram analysis suggested a lack of geospatial coherence for the whole dataset, however, the East Midlands region showed some anisotropy. As noted, measured concentrations of ICPar-P and M3-P are particularly high in the east midlands (Fig. 6b and c), mainly in Lough Neagh & Lower Ban, Foyle, Lough Swilly, Newry, Fane, Glyde and Dee, and Boyne WFD catchments (Fig. 5b). As a validation proxy the M3-P and ICPar-P data can be visually compared to the Irish Environmental Protection Agency (EPA) Priority Action Areas/Catchments, identified in Pollution Impact Potential models (PIPS, see SI). PIPS model maps are developed by identifying hydrologically sensitive areas, agricultural loading (bovine, sheep and crop data) and delivery paths and points in areas that have a high proportion of poorly-drained soils and also contain hydrological pathways to poor-status watercourses (EPA, 2019, see SI). Such areas are identified as critical source areas, which are present in the East Midlands region; Newry, Fane, Glyde and Dee, Boyne, Sligo Bay & Drowse.

Therefore, It is reasonable to infer in areas identified by ICPar-P and M3-P analyses as having high labile P contents that i) potentially there are areas of high-P-fixing behaviour combined with high labile P that can be corrected through management changes/nutrient action plans, and ii) incorporation of soil P behaviour alongside STP in risk assessment modelling such as the EPA PIPS model for the whole of Ireland, could be beneficial to developing mitigation strategies. Furthermore, the Morgan's P test does not independently identify these soils but M3 could be recommended for high P-fixing soils to provide more sustainable management.

Finally, this exercise was not intended to predict P concentration as inputs and plant offtakes will dictate this in highly managed landscapes. Therefore, the interpolation methods were only intended to understand the behaviour of P with using M3-Al as a sorption indicator. M3-Al does show geospatial continuity, however, Morgan's P and M3-P do not. The relationship between the two were provided by ANOVA analysis (Fig. 4), and therefore, P maps are only visual aids depicting this, and are not to be shown as exact concentration or predictions.

5. Conclusions

Visualising soil P behaviour based on high-resolution regional soil sampling can provide information to improve decision making around P management and water quality protection. They can also help identify areas with the potential for P loss from soil so that water quality measures can be more targeted and effective. Maps of soil P concentration in the northern part of Ireland do not reflect geogenic control of P distribution, rather suggesting that anthropogenic inputs may mask any underlying geological processes. Mapping the soil P index together with M3-Al concentration can help characterise soil P behaviour at regional scales, providing spatial information to help achieve more sustainable P use to i) avoid increasing labile P pools or ii) identify areas where P is likely to remain in the solution phase and thus be at risk of loss to local watercourses.

Interpolated maps provide a basis for mapping spatially coherent areas of dynamic mechanisms of P behaviour. Using M3-Al derived P-sorption indicators could be extended to achieve national/European coverage, and deployed to provide national scale data for monitoring and assessment. In soils that have high P-fixing potential the interpolated maps show differences between the measured Morgan's P and P index and ICPar-P and M3-*P* values. Mapping P sorption behaviour on a large scale can help to identify areas that could benefit from targeted management approaches. In soils that have Low P-fixing potential, there are clear regional trends where over-application of P could potentially lead to loss of P and pollution of water courses. Mapping these data on a national basis could be used to analyse spatial trends and behaviours of P, in order to align with the WFD and Soil Health Law to achieve agronomic sustainability and reduce the impact of incidental P loss on the environment. Furthermore, including M3 analysis alongside Morgan's P in nutrient action plans can help identify whether or not fields are in the high P-fixing category and thus inform P management.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has been used.

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Appendix A. Supplementary data

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