Journal of Hydrology 634 (2024) 131052

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Regional scale evaluation of nitrate fluctuations in groundwater using cluster analysis and standardised hydrometeorological indices

M.J. Ascott [a,*], D.C. Gooddy [a], B. Marchant [a], N. Kieboom [b], H. Bray [c], S. Gomes [d]

[a] British Geological Survey, Maclean Building, Benson Lane, Crowmarsh Gifford, Oxfordshire OX10 8BB, UK
[b] Environment Agency, Horizon House, Deanery Road, Bristol BS1 5AH, UK
[c] Environment Agency, Rivers House, East Quay, Bridgwater TA6 4YS, UK
[d] Environment Agency, Orchard House, Endeavour Park, London Road, Addington, West Malling, Kent, ME19 5SH, UK

ARTICLE INFO

Keywords:
Nitrate
Groundwater
Standardised hydrometeorological indices
Time series analysis

ABSTRACT

Temporal fluctuations in nitrate in groundwater can result in concentrations temporarily exceeding drinking water standards. This can bring about the need for costly water treatment or blending. Despite this, the extent and potential controls on these fluctuations are poorly understood, particularly at regional to national scales. Applied to Southeast England (UK), here we develop the first application of cluster analysis and standardised hydrometeorological indices to evaluate nitrate fluctuations in groundwater at the regional scale. Hierarchical and K-means cluster analysis of 96 groundwater nitrate time series for the period 1995–2022 showed that nitrate time series can be divided into 4 clusters: (1) long term increasing trends ($n = 23$, mean trend = 0.26 mg NO_3/l/a), (2) long term decreasing trends ($n = 19$, mean trend = − 0.65 mg NO_3/l/a), (3) long term increasing trends with seasonal fluctuations ($n = 24$, mean trend = 0.29 mg NO_3/l/a) and (4) long term increasing trends superimposed on near-decadal scale fluctuations ($n = 30$, mean trend = 0.22 mg NO_3/l/a). Boreholes in cluster 1 appear to be deeper than boreholes in cluster 2. In comparison to shallower boreholes, deeper boreholes are likely to be intersecting longer groundwater flow systems where nitrate concentrations are affected by historic "legacy nitrate" leaching. There is weak spatial coherence in the clustering, with clusters 3 and 4 present in the South and North Downs respectively. Cross-correlation analysis between groundwater nitrate time series with precipitation and groundwater level indices showed that rapid seasonal fluctuations in nitrate concentrations in cluster 3 in the South Downs are associated with rapidly responding groundwater level fluctuation. This is likely due to the highly fractured and faulted nature of the Chalk aquifer in this area. This is in contrast with the slower near-decadal fluctuations in cluster 4 in the North Downs. The strongest correlations between groundwater levels and nitrate concentrations in cluster 3 occurred when cross-correlating at a lag of zero months, which would suggest that matrix diffusion is unlikely to be a significant control on nitrate seasonality. Seasonal fluctuations in nitrate concentrations are likely to be associated with a combination of piston displacement at the water table and changing groundwater flow paths to the borehole. Future climate change may change the magnitude and timing of seasonal fluctuations caused by these processes. The methodology developed here is generic and can be applied wherever there is a large body of groundwater nitrate time series data.

1. Introduction

Nitrate (NO_3) is considered the most widespread pollutant in groundwater (Abascal et al., 2022). Elevated concentrations of nitrate in groundwater cost billions of dollars per year globally associated with impacts on surface water ecosystems and the need to treat high nitrate water for drinking (Dodds et al., 2009; House of Commons Environmental Audit Committee, 2018; Pretty et al., 2000). Despite decades of effort to reduce NO_3 losses from agricultural sources across many developed countries (e.g. the UK, USA, EU-27 countries), nitrate concentrations in groundwater are often still continuing to increase (Musacchio et al., 2020; Stuart and Lapworth, 2016; Van Meter et al., 2018). This is due in part to the "legacy effect", where time lags in the unsaturated zone and saturated zone mean it can take decades for the impacts of reductions in NO_3 losses to be observed in groundwater (Ascott et al., 2017a; Ascott et al., 2016; Wang et al., 2016).

* Corresponding author.
E-mail address: matta@bgs.ac.uk (M.J. Ascott).

https://doi.org/10.1016/j.jhydrol.2024.131052
Received 23 August 2023; Received in revised form 5 February 2024; Accepted 21 February 2024
Available online 11 March 2024

In addition to long term trends, fluctuations in nitrate concentrations in groundwater over seasonal to decadal scales are also important. Seasonal peaks in nitrate can be particularly problematic, as these can temporarily exceed drinking water standards resulting in the need for temporary treatment or water blending. These temporary exceedances can typically occur before exceedances associated with long term trends (Stuart et al., 2009). Moreover, seasonal variability itself can also obscure long term trajectories in nitrate related to changes in nitrate losses from soils (Rozemeijer et al., 2009). Seasonal peaks exhibit a first order hydrometeorological control (i.e. presence of winter rainfall and recharge), with a range of local processes (e.g. piston flow, bypass flow, changing saturated zone flow paths) controlling responses in individual boreholes (Stuart et al., 2009). Changes in seasonal variability in nitrate concentrations have also been postulated to occur in the future associated with climate change (Stuart et al., 2011). Previous work exploring the extent of, and controls upon, temporal fluctuations in nitrate in groundwater at the regional scale is scant. Most work has evaluated nitrate fluctuations over relatively small spatial scales. This includes assessments for individual boreholes (Sorensen et al., 2015; Stuart et al., 2009), or for small numbers of boreholes and springs at the farm (Huebsch et al., 2014; Rozemeijer et al., 2009), city (Kawagoshi et al., 2019; Li et al., 2015) or catchment (McAleer et al., 2022; Smith et al., 2010) scale. At the national scale, Stuart et al. (2007) evaluated trends in groundwater nitrate concentration data in England (UK), and made an assessment of seasonality. However, Stuart et al. (2007) did not assess decadal scale variability, nor did they evaluate the controls on fluctuations, nor did they assess the spatial distribution of the modes of fluctuation. At the basin scale, Roy et al. (2007) evaluated nitrate trends and variability in six groundwater bodies in the Hampshire Basin, England. Roy et al. (2007) used the Grath et al. (2001) methodology, where monthly mean nitrate concentrations are calculated for each sampling point, and these are then averaged for all sampling points in a groundwater body. This methodology has been reported to be sound, but will obscure any systematic variability within groundwater bodies and can be sensitive to missing data (Stuart et al., 2007). Recently, Jutglar et al. (2021) evaluated changes in nitrate concentrations in groundwater at the regional scale in southwest Germany following recovery from drought conditions. Jutglar et al. (2021) focussed on the 2003 drought in Europe, and argued that further work is required to understand nitrate flushes following droughts and their consequences. Whilst other workers have evaluated long term trends in nitrate in groundwater at national (Hansen et al., 2011; Rupert, 2008) and regional scales (César et al., 2014; Hudak, 2000), these have not considered fluctuations at seasonal and decadal time scales. To date, no work at the regional scale has characterised seasonal and decadal fluctuations and long term trends in nitrate concentrations using individual groundwater nitrate time series, and how these vary spatially.

In order to characterise temporal fluctuations across many monitoring locations, methodologies to standardise hydrometeorological time series have been developed. These methods use a statistical distribution to transform raw hydrometeorological time series data to a "standardised" index, defined as having mean of zero and a standard deviation of 1. Methods have been applied to numerous variables related to water resources (standardised precipitation index (SPI) (McKee et al., 1993), standardised precipitation-evapotranspiration index (Vicente-Serrano et al., 2010), standardised streamflow index (Svensson et al., 2017)), and in the past decade, this approach has been also extended to groundwater resources (standardised groundwater level index (SGI) (Bloomfield and Marchant, 2013). The SGI has been used to assess groundwater drought in the UK (Bloomfield et al., 2015; Bloomfield and Marchant, 2013; Bloomfield et al., 2019) and internationally for resource assessments (Ascott et al., 2020; Sorensen et al., 2021). These studies used a deseasonalised SGI, where SGI represents the variation in groundwater levels relative to the seasonal norm. A variant of the SGI that includes seasonal component has also been used in assessments of groundwater flooding (Ascott et al., 2017b). For further information on the SGI methodology the reader is referred to Bloomfield and Marchant (2013).

The SGI has typically been used in combination with cluster analysis. Whilst cluster analysis of groundwater quality data has been undertaken for decades (see recent reviews by Patel et al. (2023) and Muniz and Oliveira-Filho (2023)), previous studies have used cluster analysis as a tool to group multivariate groundwater quality data that are time invariant. Zanotti et al. (2023) recently reported the first application of time series clustering to groundwater quality data, which showed the method to be useful for mapping temporal patterns of chlorinated solvent contamination at the city scale. To date, no study has combined the use of clustering of groundwater quality time series (including nitrate) with standardised hydrometeorological indices. Nitrate is one of the most widely monitored groundwater contaminants (Lapworth et al., 2022), with concentrations regularly monitored by environmental regulators and water utilities for decades in many countries (Musacchio et al., 2020; Roy et al., 2007). Nitrate time series are a large body of data in which the combined use of cluster analysis and standardised indices affords significant potential to improve the understanding of temporal fluctuations in groundwater nitrate concentrations.

The objective of this paper is to characterise the different modes of temporal fluctuations in nitrate concentrations in groundwater at the regional scale, and to explore potential controls on these fluctuations. To do this we develop the first application of standardised indices and cluster analysis to classify groundwater nitrate time series across southeast England (UK). We then evaluate relationships between the standardised nitrate time series and standardised hydrometeorological indices to explore controls on modes of fluctuation. The implications of this are then considered in light of future climate change. The cluster analysis is shown to be a useful tool in mapping different patterns in temporal nitrate fluctuations. The methodology developed is generic and can be applied wherever there is a large body of groundwater nitrate time series.

2. Materials and methods

2.1. Study area

The study area for this research is southeast England (UK), as shown in Fig. 1. In the study area there are three principal bedrock aquifers; the Great Oolitic limestones, the Lower Greensands and the Chalk (Allen et al., 1997). The Chalk is also in hydraulic continuity with a locally important minor aquifer, the Upper Greensands and they are usually considered together as a single aquifer unit (Jones et al., 2000). These aquifers provide a substantial component of public water supply in the region (Ascott, 2017) and support baseflow to groundwater dependent terrestrial ecosystems and rivers (Rangeley-Wilson, 2021).

Nitrate contamination of groundwater is a significant issue in England. Based on 191 time series of variable record length (5 to 43 years), Stuart et al. (2007) estimated a median annual average trend in nitrate concentrations in groundwater in England of 0.34 mg NO_3/l/a. In 2000 over a third of sites exceeded the 50 mg NO_3/l drinking water standard. Within England, the southeast is particularly affected associated with large areas of agricultural land and unconfined aquifer systems (Ascott et al., 2019), resulting in the majority of the study area being designated a nitrate vulnerable zone (Environment Agency, 2019).

2.2. Data collation, pre-processing and filtering groundwater nitrate time series

Groundwater nitrate time series from boreholes and springs in the study area were extracted from the English environmental regulator's Water Information Management System (WIMS) database. Only data collected for the purposes of long term environmental monitoring by the environmental regulator and by water supply companies were selected to avoid extracting data collected during short term pollution

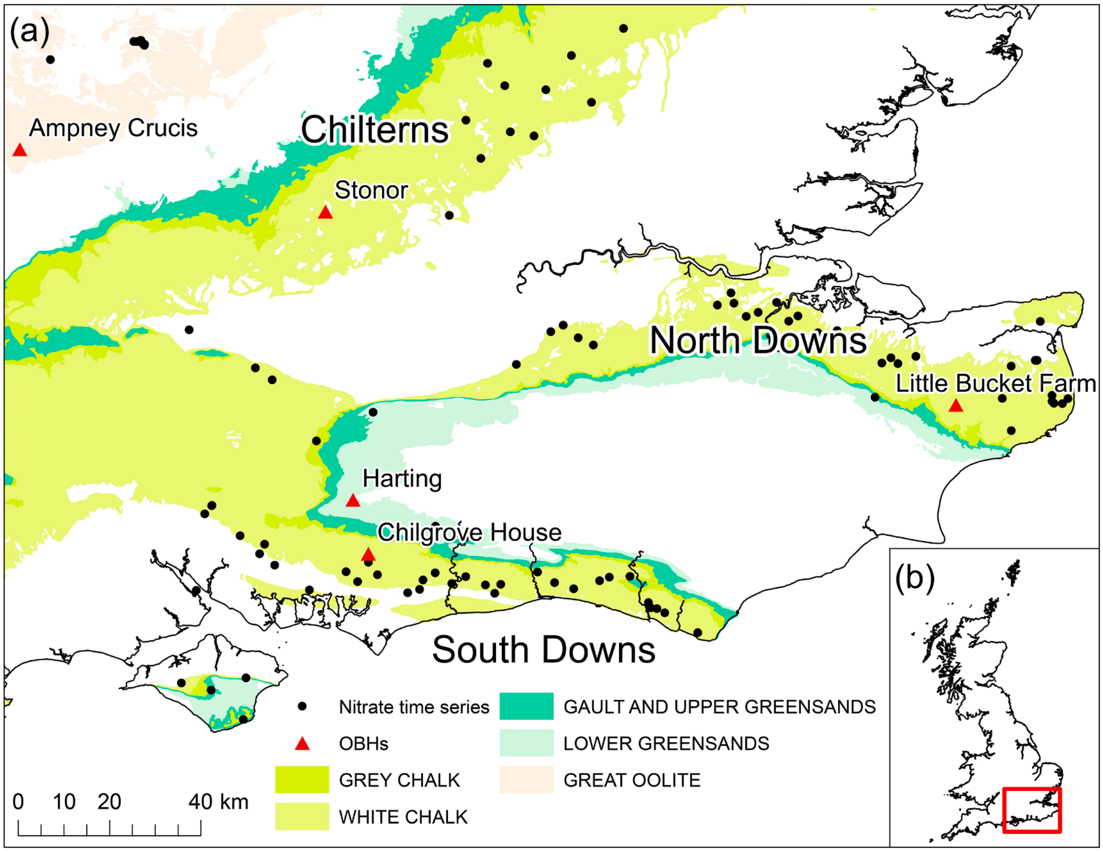

Fig. 1. (a) Location of groundwater nitrate time series and observation boreholes (OBHs) overlain on 1:625,000 scale bedrock geology for principal aquifers in the study area, and (b) location of study area in Great Britain. Contains OS data © Crown copyright and database rights 2023.

investigations. Data were extracted for nitrate as NO_3 (n = 93,164) and as N (n = 126,535). Where there were samples with only nitrate as NO_3 present, these were converted to nitrate as N. Data from sampling points containing the strings "TREATED" (19 sample points) or "FINAL" (indicating water samples taken after final treatment, 9 sample points) in the sampling point name were removed.

To characterise both short term nitrate fluctuations and long term trends, time series that are relatively regularly sampled and covering at least 2 decades were required. We therefore subsetted the nitrate data using a set of bespoke criteria building existing work on nitrate time series trends (Stuart et al., 2007) and guidance on time series characterisation of natural variability in hydroclimate (World Meteorological Organization, 2017). Stuart et al. (2007) used a minimum of 5 years of data for each time series and a regularity index R (the ratio of the mean to the standard deviation of the gap between measurements) of 0.5, and a minimum of 20 measurements for each time series. These are too short to evaluate decadal scale variability. World Meteorological Organization (2017) guidelines recommend that at least 30 years of data should be used for characterisation of natural variability at decadal time scales. Application of this threshold along with $R = 0.5$ and on average 1 sample per month resulted in only 19 time series meeting the criteria. We therefore relaxed the criteria to the following: 20 years of data with $R = 0.5$ and on average, 1 sample per month. This resulted in 96 time series meeting the criteria. The locations of these time series are shown in Fig. 1 and Table S1. This represents a balance between use of only long time series and an acceptable spatial coverage of time series across the study area. Of the 96 time series, 84 are from boreholes and wells and 12 are from springs. All are located at outcrop in unconfined aquifers where denitrification has been shown to be insignificant (Rivett et al., 2008). 83 time series are from samples taken from the Chalk (2 of which are also from the Upper Greensands), 3 are from the Lower Greensands and 10 are from the Oolitic Limestones.

2.3. *Standardisation and clustering of groundwater nitrate time series*

Measurements in the groundwater nitrate time series where concentrations were below the limit of detection were set to half of the limit of detection (0.196 mg N/L). Across all 96 time series this applied to 0.62 % of the data in total. For each of the 96 time series we resampled nitrate concentration values to monthly means to avoid biases in the number of samples per unit time. Across all 96 time series the first measurement was in January 1989, and the most recent measurement was in June 2022. We then plotted a "missingness" heatmap to evaluate the extent of missing data across all the time series (Fig. S1). This showed that there was missing data between 1989 and 1995 for many of the time series, and so we further sub-sampled the data by truncating the start and end of all the time series to 1995 to 2021 respectively, to ensure most sites had regularly sampled data (Fig. 2). Data outside of this period were not considered further. Across all the time series, there are c. 74 % data present. Missing values were imputed by linear interpolation. We then standardised the data for each time series such that mean = 0 and standard deviation = 1. This means that the cluster analysis was unaffected by differences in the absolute magnitude of nitrate concentrations between the sites. As characterisation of seasonal changes in nitrate are an aim of this research, in contrast to the SGI (Bloomfield and Marchant, 2013), our approach intentionally does not remove seasonality nor do we force the standardised time series to a normal distribution.

We used a cluster analysis approach to assess how standardised nitrate time series vary spatially across the study area. To determine the most appropriate number of clusters, we first undertook hierarchical clustering using Euclidean distance and the complete linkage method

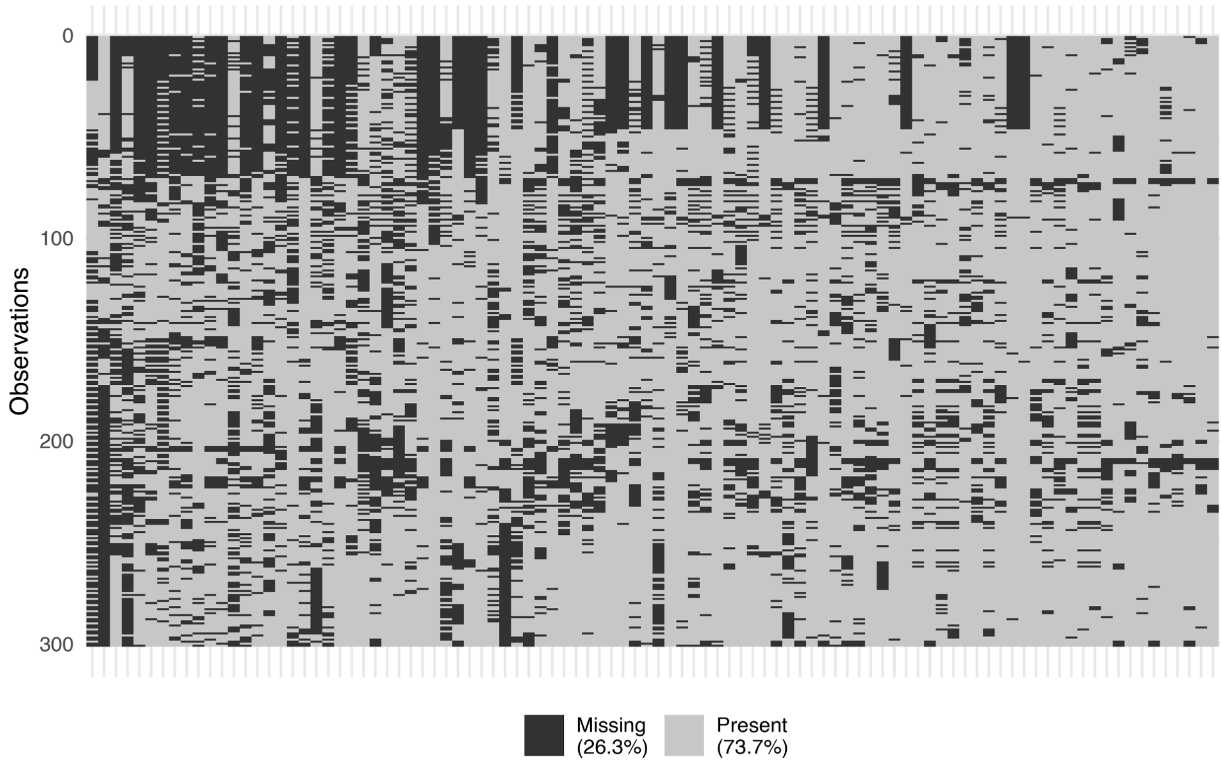

Fig. 2. "Missingness" plot for all nitrate time series that met the filtering criteria for 1995–2020. Each column represents a nitrate time series, and each row (observation) is a month from March 1995 - March 2020. Columns are ordered from left to right from least to most complete.

(Webster and Oliver, 1990) to produce an ordered heatmap and cluster dendrogram. We also undertook k means clustering for k = 1 to 15 to and estimated the within clusters sum of squares to produce the k means "elbow" plot. The choice of the number of clusters can be somewhat subjective. In the clustering of groundwater level hydrographs, Bloomfield et al. (2015) used a rule-based approach to identify the smallest number of clusters that resolve the spatial distribution of hydrogeological characteristics across a region. A similar approach was also used in the clustering of groundwater flooding indices by Ascott et al., (2017b). In this study, we build on the approaches of Bloomfield et al. (2015) and Ascott et al., (2017b) to develop a set of criteria for clustering groundwater nitrate time series. Using expert hydrogeological judgement, we identified the smallest number of clusters that resolved the following characteristics of groundwater nitrate time series: (1) the overall trajectory of time series (increasing or decreasing trends), (2) the presence of seasonal and decadal scale variability, (3) the presence of any spatial coherence in the cluster membership (how time series are split between different clusters). Use of these criteria in conjunction with evaluation of the ordered heatmap, cluster dendrogram and "elbow" plot (Fig. S4) showed a suitable number of clusters was k = 4. We then repeated the k means cluster analysis with k = 4, and initialising using 10,000 random sets as starting centres and then picking the best starting set. We plotted the individual time series by cluster and the cluster centres, and mapped the cluster membership across southeast England. To ensure the clustering was not unduly affected by missing data, we also repeated the hierarchical cluster analysis for a smaller subset of data over 2000–2020 (see Fig. S2). This produced the same overall cluster membership (Fig. S3) as when clustering using data for 1995 to 2020 (Fig. 3).

2.4. Evaluation of temporal variability and trends between nitrate time series clusters

For each nitrate time series we calculated recent trends using a linear model using the decimal year of sampling as the independent variable. In comparison to non-linear methods (e.g. Mann-Kendall, Generalised Additive Models), this method simplifies and aids interpretation of long term trends by separating the linear component. The approach has previously been applied to groundwater nitrate time series (Stuart et al., 2007) and is also advantageous as missing data can be accommodated in the method. Visual inspection of the cluster centroids (Fig. 4) showed that trends over 1995–2000 are anomalous in comparison to recent behaviour, potentially associated with the larger number of sites with missing data over this period (Fig. 2). We therefore calculated trends for 2000–2020. Five potential controls on temporal variability between nitrate time series clusters were then evaluated related to borehole construction and hydrometeorological setting; borehole depth, monthly precipitation totals, the standardised precipitation index (SPI), monthly mean groundwater levels and the standardised groundwater level index (SGI). For each of the nitrate time series we extracted borehole depth from a separate database of borehole, well and spring metadata held by the English environmental regulator. These potential controls were selected as (1) the focus of this study is the relationships between hydrometeorological variability and change and seasonal/decadal responses in groundwater nitrate time series, (2) there is very limited variation in aquifer type (see section 2.2 and Fig. 1) across the sites, (3) detailed information regarding borehole construction apart from borehole depth (see above) were not available (e.g. depth of casing, casing diameter) and (4) historical land use change associated with each borehole's catchment area were not available.

For each time series we extracted monthly precipitation totals in mm/month from the 1 km gridded HadUK-Grid dataset (Hollis et al., 2023). Bilinear interpolation was used so that for each site, values were interpolated from the four nearest raster cells. We calculated cross-correlations between the detrended standardised monthly nitrate time series with the monthly precipitation totals for each site. Detrending was undertaken by calculating a least-squares fit of a straight line to the data and subtracting the resulting function from the data. Cross correlations were calculated by forward shifting the nitrate time series (known herein as lag) by 0 to 10 months, and we recorded the maximum value of the Pearson's correlation coefficient and the accompanying lag. For the monthly precipitation totals extracted from HadUK-Grid, we then calculated SPI summing precipitation totals for accumulation periods of 1 to 48 months (McKee et al., 1993). For each site, we cross-correlated the detrended standardised monthly nitrate time series with SPI-1 to SPI-48. The maximum correlation between nitrate and SPI was recorded with the associated SPI accumulation period (in months) and lag.

To correlate nitrate time series with groundwater level time series, each site had to be related to an observation borehole. Groundwater level time series for sampled boreholes were not available. Consequently, each site was linked to an observation borehole used in monthly hydrological reporting (Mackay et al., 2015). The locations of the nitrate time series and the corresponding observation boreholes are shown in Fig. 1 and Table S1. These boreholes are known to have minimal influence from groundwater abstraction (Prudhomme et al., 2017) and therefore represent a reasonable proxy for the groundwater level status across regions of the Chalk, Lower Greensands and Oolitic limestone aquifers of southeast England. We extracted monthly mean groundwater level time series for each observation borehole, and cross correlated detrended standardised monthly nitrate concentrations with standardised groundwater levels (mean = 0, standard deviation 1, note this is not the same as the SGI as developed by Bloomfield and Marchant (2013), which is deseasonalized), and recorded the maximum value of the Pearson's correlation coefficient and the accompanying lag. The same methodology was then repeated for correlations between detrended standardised monthly nitrate concentrations with SGI (using 1995–2022 as a reference period).

For each groundwater nitrate time series, the methodology above produces a number of metrics describing the time series (trend) and relationships to borehole construction (borehole depth), precipitation (precipitation correlation, precipitation lag, SPI correlation, SPI accumulation period, SPI lag) and groundwater level (groundwater level correlation, groundwater level lag, SGI correlation, SGI lag). To assess how these metrics vary between clusters, we calculated mean values for each cluster. Five of the 11 metrics were non-normally distributed ($p < 0.05$, Shapiro-Wilk test, see Table 1). We therefore assessed if there are significant differences in means of the metrics between the clusters using the non-parametric Kruskal Wallace test. Where there were significant differences, we determined which pairs of clusters were significantly different using a Wilcoxon rank sum test with continuity correction. We plotted boxplots of borehole depth by cluster, and scatter plots of precipitation, groundwater level and SGI lags and correlation coefficients as a function of cluster membership. Boxplots and scatterplots were also used to visualise differences between the clusters related to SPI-Nitrate correlations, SPI accumulation periods and SPI lags. All analysis of data was undertaken using the statistical computing environment R (R Core Team, 2022). The packages "stats", "pracma" and "spei" were used for the cluster analysis, detrending and calculation of SPI for the correlation analysis respectively.

3. Results

3.1. Cluster analysis

Fig. 3 shows the heatmap and dendrogram derived by hierarchical cluster analysis of the standardised nitrate time series. A first order control on cluster partition (i.e. k = 2) appears to be whether sites show an overall positive or negative trend over time. Broken down further, visually the time series can be grouped as follows: sites that show near-linear increases through time; sites that show near-linear decreases through time; sites with seasonal behaviour superimposed on a long-term increasing trend; and sites with decadal behaviour superimposed on a long-term increasing trend. Fig. 4 shows the centroids and individual standardised nitrate time series for each cluster when applying the k-means method for k = 4. The cluster centroids show the same overall pattern as the hierarchical cluster analysis results. For the rest of this analysis, the clusters will be referred to as follows based on Fig. 4:

- Cluster 1 – a long term increasing trend (mean trend (2000–2020) = 0.26 mg NO_3/l/a)
- Cluster 2 – a long term decreasing trend (mean trend (2000–2020) = -0.38 mg NO_3/l/a)
- Cluster 3 – seasonal variability and increasing trend (mean trend (2000–2020) = 0.29 mg NO_3/l/a)

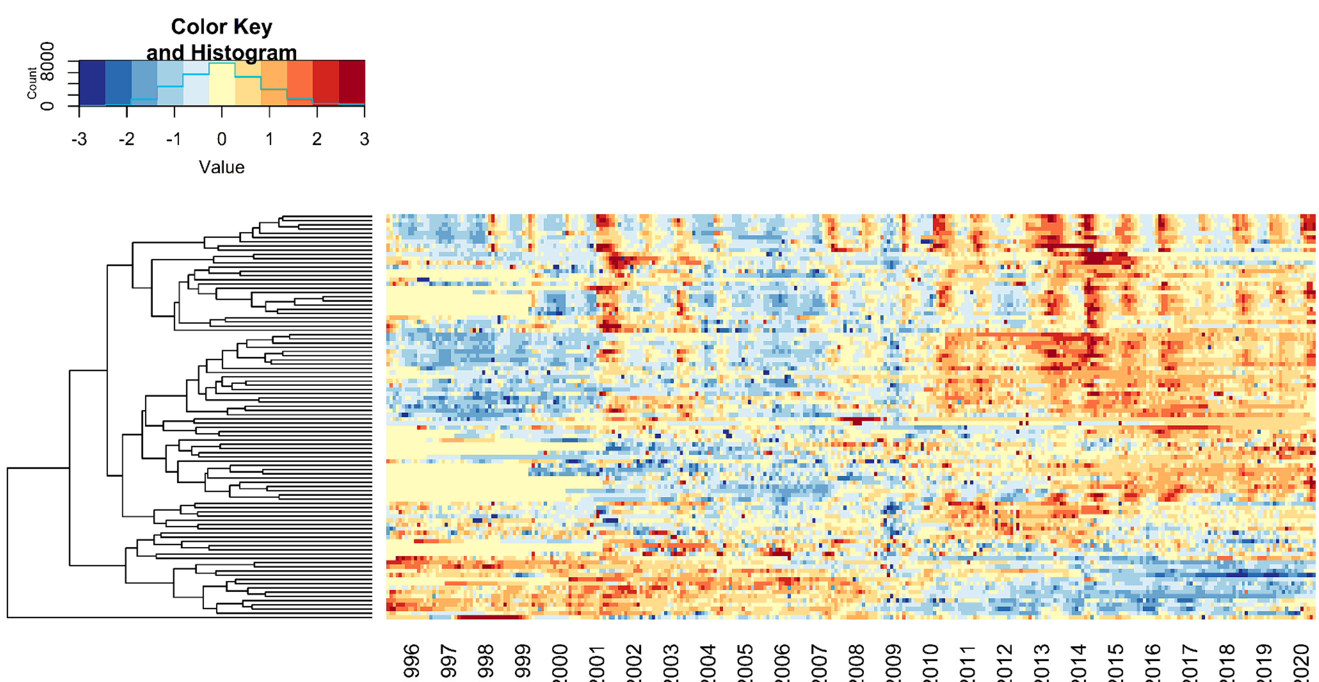

Fig. 3. Heatmap and dendrogram for standardised groundwater nitrate time series for 1995–2020. Red and blue colours indicate higher and lower concentrations respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

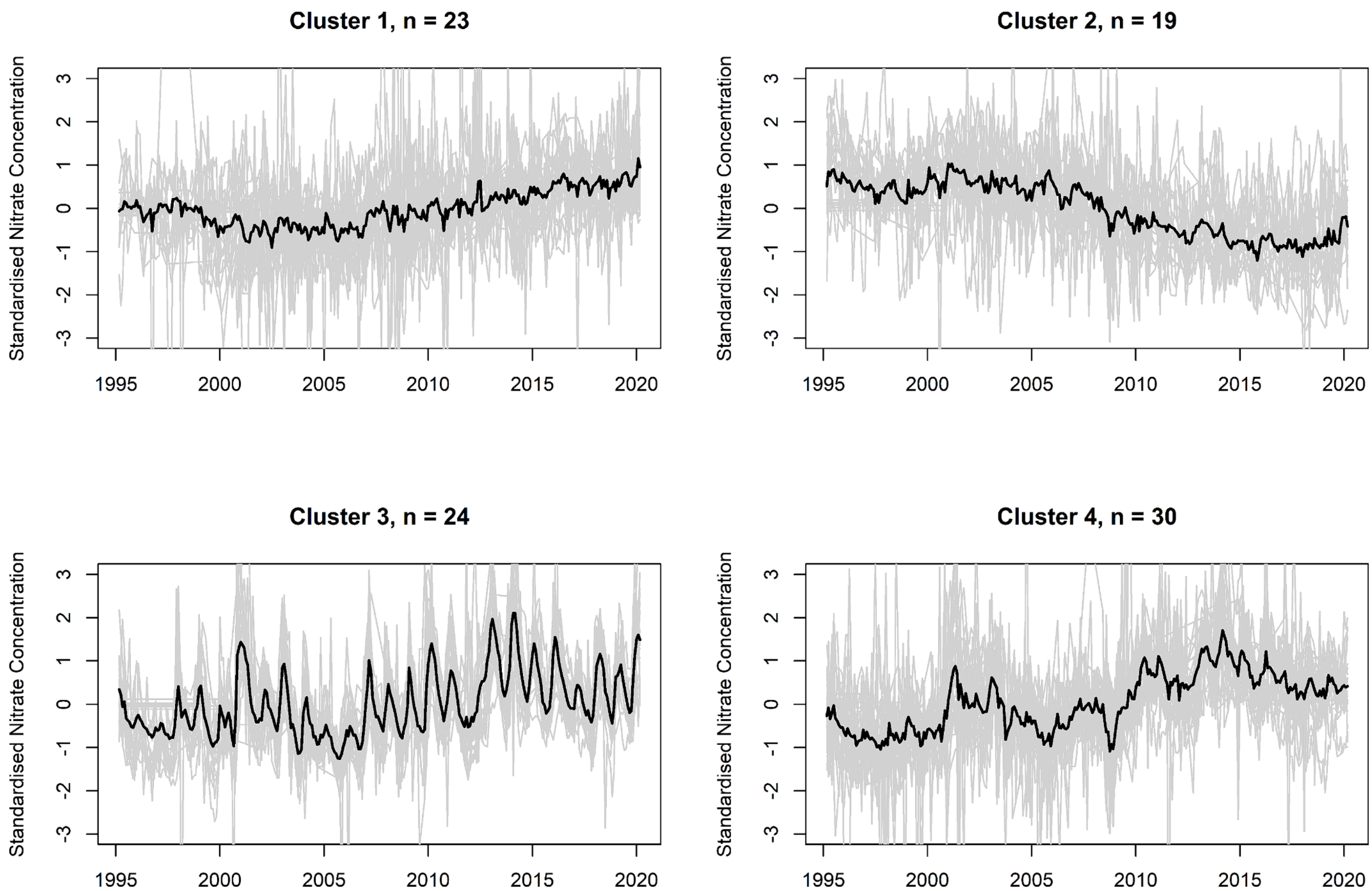

Fig. 4. Standardised nitrate time series for cluster centroids (black) and individual time series within each cluster (grey), for k = 4.

- Cluster 4 – decadal-scale variability and increasing trend (mean trend (2000–2020) = 0.22 mg NO_3/l/a)

Whilst there is considerable spread, the overall pattern within each cluster is the same as the centroid (e.g. all the time series in cluster 3 show seasonal behaviour, all the time series in cluster 2 show decreases). The trend in cluster 2 is significantly different ($p < 0.05$, Wilcoxon rank sum test, see Table 1) than the other clusters.

Fig. 5 shows the spatial distribution of the cluster membership in the context of 1:625,000 scale bedrock aquifers of southeast England. There is no strong spatial coherence to the cluster membership, although visually it appears that cluster 3 may be predominantly in the South Downs and cluster 4 in the North Downs. Of all the sites in cluster 3, 75 % are with the South Downs. Of all the sites in cluster 4, 57 % are in the North Downs. All 10 Oolitic Limestone sites are in cluster 2, with the 83 Chalk and 3 Lower Greensands sites spread across all 4 clusters.

3.2. *Relationships between clusters, borehole depth, precipitation and groundwater level indices*

Table 1 shows mean values for nitrate time series metrics for each cluster. Whether the metrics are normally distributed is indicated by the Shapiro-Wilk p-value. Whether there are significant differences between the clusters for each metric is indicated by the Kruskal Wallace Test p-value. If there are significant differences, the pairs of clusters are shown (based on Wilcoxon rank sum test with continuity correction).

Fig. 6 shows the relationship between borehole depth and the four clusters. Whilst the mean borehole depth for cluster 2 (64 m) is smaller than clusters 1, 3 and 4 (80–95 m), there is substantial overlap in the distribution and no significant differences between the clusters (Table 1). Of the nitrate time series for springs (n = 12), 75 % (n = 9) are in cluster 2, with the remainder (n = 3) in cluster 3.

Fig. 7 shows the correlation coefficients and lags for cross-correlations between detrended standardised monthly nitrate concentrations and monthly precipitation totals (left), groundwater levels (centre) and SGI (right), as split by cluster. Cluster 3 has significantly stronger correlations with precipitation, GWL and SGI than the other clusters (Table 1), with the next strongest correlations in cluster 4. Clusters 1 and 2 are generally poorly correlated ($r < 0.2$, $p > 0.05$) with precipitation, GWL and SGI, with a wide range of lags for maximum correlation. These clusters are not considered further in these results. For clusters 3 and 4, correlations between detrended standardised nitrate concentrations and GWLs (mean r = 0.63 and 0.33 respectively) are greater than for correlations with precipitation (mean r = 0.39 and 0.17) or SGI (mean r = 0.40 and 0.30), see Table 1. For cluster 3, correlations with GWLs and SGI are less lagged (mean lag = 0 months) in comparison to correlations with precipitation (mean lag = 3 months). There is also less difference in the magnitude of the correlation coefficients between cluster 3 and cluster 4 when correlating with SGI (difference in mean r = 0.1) in comparison to correlating with GWLs (difference in mean r = 0.30).

Fig. 8 shows SPI-standardised nitrate correlation coefficients (left), SPI accumulation period (middle), and SPI lag (left) split across the four clusters. Cluster 3 has significantly stronger correlations (mean r = 0.47) between SPI and standardised nitrate than cluster 4 (mean r = 0.36). Cluster 3 (mean SPI accumulation period = 15 months, mean SPI lag = 0 months) has a significantly smaller magnitude of SPI accumulation periods and lags than cluster 4 (mean SPI accumulation period = 23 months, mean SPI lag = 2 months).

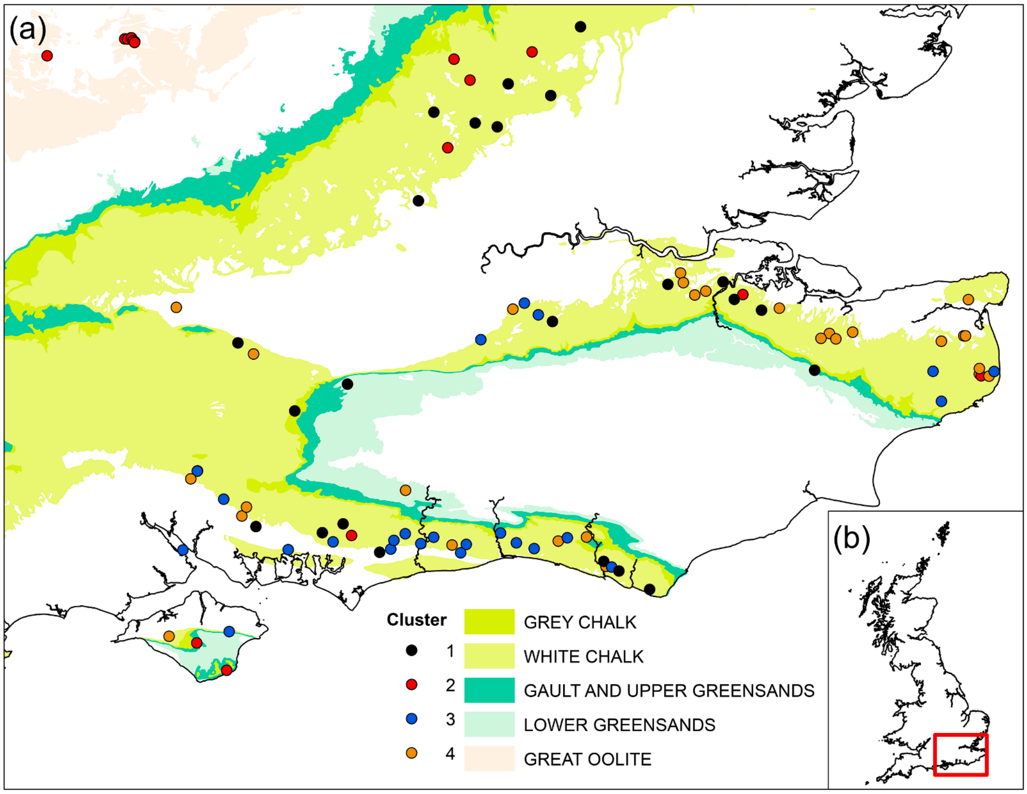

Fig. 5. (a) Spatial distribution of nitrate clusters overlain on 1:625,000 scale bedrock geology for principal aquifers in the study area and (b) location of study area in Great Britain. Contains OS data © Crown copyright and database rights 2023.

Table 1
Mean values for nitrate time series metrics for each cluster, Shapiro-Wilk normality test p-values, Kruskal Wallace Test p-values and significant ($p < 0.05$) pairwise differences between clusters (Wilcoxon rank sum test with continuity correction).

Metric	Unit	Cluster mean				Shapiro-Wilk Test p-value	Kruskal Wallace Test p-value	Significant pairwise differences
		1	2	3	4			
Trend	mg NO_3/l/a	0.26	−0.38	0.29	0.22	<0.05	<0.05	2–1, 2–3, 2–4
Borehole depth	(m)	94.99	63.96	79.16	85.63	0.36	0.19	NA
Precipitation correlation	(-)	0.07	0.14	0.39	0.17	0.25	<0.05	1–2, 1–3, 2–3,2–4, 3–4
Precipitation lag	Months	4.22	6.00	2.71	5.43	0.18	<0.05	2–3, 3–4
SPI correlation	(-)	0.15	0.21	0.48	0.36	0.51	<0.05	1–3, 1–4, 2–3, 2–4, 3–4
SPI accumulation period	Months	18.09	14.10	15.33	23.20	<0.05	<0.05	2–4,3–4
SPI lag	Months	3.70	4.00	0.14	1.87	<0.05	<0.05	1–3, 2–3, 3–4
GWL correlation	(-)	0.05	0.19	0.63	0.33	0.86	<0.05	1–2, 1–3, 1–4, 2–3, 2–4, 3–4
GWL lag	Months	4.09	2.70	0.19	1.83	<0.05	<0.05	1–3, 2–3, 3–4
SGI correlation	(-)	0.01	0.11	0.40	0.30	0.50	<0.05	1–2, 1–3, 1–4, 2–3, 2–4, 3–4
SGI lag	Months	3.61	4.00	0.29	3.30	<0.05	<0.05	1–3,2–3, 3–4

4. Discussion

4.1. *Controls on historic groundwater nitrate fluctuations*

The results in section 3.2 provide insights into the overarching controls on historic temporal changes in groundwater nitrate fluctuations and the role of climate variability at the regional scale. Clusters 1 and 2 show long term increasing and decreasing nitrate trends respectively. Boreholes in cluster 1 appear to be deeper than in cluster 2 (Fig. 6). In southern England nitrate leaching peaked in c. 1980 (Wang et al., 2016) and subsequently declined. However, Stuart et al. (2007) showed long term increasing trends in nitrate in groundwater. This discrepancy is due to the multidecadal scale time lags between nitrate leaching at the base of the soil zone and concentrations in groundwater due to long travel times in the unsaturated and saturated zones. Deep boreholes in cluster 1 are likely to have long unsaturated and saturated zone travel times, resulting in increasing nitrate trends reflecting the historic "legacy nitrate peak". In contrast, shallow boreholes in cluster 2 may be intercepting groundwater flow with more rapid travel times due to thinner unsaturated zones and shorter saturated zone pathways. This is further supported by the nitrate time series for springs present in cluster 2 (75 % of the spring time series in the data), where these springs may be sourcing water from shallower groundwater flow systems. In these shallower systems, borehole and spring flows are likely to be sourced from more recently recharged groundwater with lower nitrate concentrations in comparison to deeper boreholes.

Superimposed on a long-term increasing trend, clusters 3 and 4 show seasonal and decadal variability respectively. The timing of seasonal and

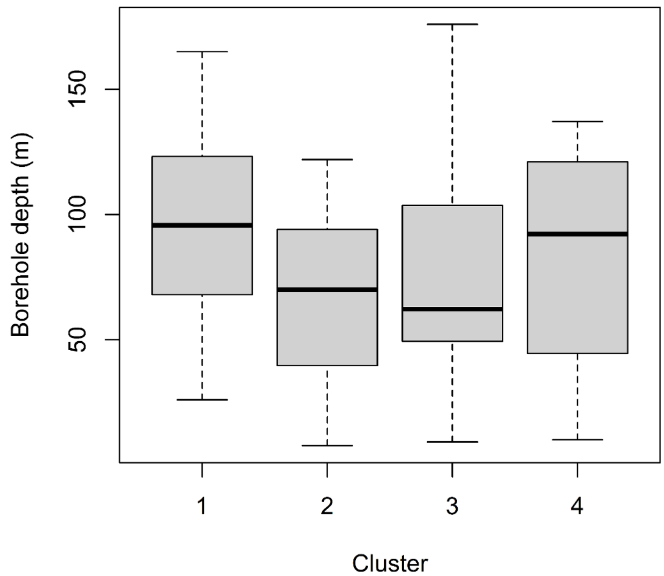

Fig. 6. Boxplot of borehole depths for the different clusters.

decadal changes in nitrate concentrations is correlated to seasonal and decadal changes in groundwater levels. There also appears to be some weak spatial coherence of the clusters with the majority of cluster 3 and 4 boreholes in the South and North Downs respectively (Fig. 5). Differences in correlations with driving variables highlight the differences between clusters. Cluster 3 correlates strongest with groundwater levels, with notably weaker correlations for cluster 4. However, when correlating with the deseasonalised SGI the differences in correlation strength between cluster 3 and 4 are small. When correlating detrended standardised nitrate concentrations with SPI, the strongest correlations for cluster 4 seem to be for longer accumulation periods and lags than for cluster 3. Marchant and Bloomfield (2018) showed that groundwater levels in the South Downs Chalk are notably flashier than in other regions (including the North Downs), associated with the high degree of faulting and fracturing (Jones and Robins, 1999). We suggest that the greater flashiness of groundwater level fluctuations in the South Downs is associated with the seasonality in nitrate concentrations in comparison to the slower responding North Downs.

This poses the question, what processes are driving the seasonal fluctuations in cluster 3 and the decadal variability in cluster 4? Stuart et al. (2009) identified 4 mechanisms that could control nitrate fluctuations in groundwater: (1) winter piston flow through the unsaturated zone matrix, (2) winter bypass flow bringing high nitrate water from the base of the soil zone directly to the water table, (3) water table rise from water entering elsewhere in the catchment flushing out porewater by matrix diffusion and (4) change in flow path giving access to a greater percentage of shallow high nitrate water. It was concluded that porewater flushing by matrix diffusion could potentially result in a lag between water table rises and nitrate concentration rises. As the strongest nitrate-groundwater level correlations for cluster 3 are for a lag of close to zero months (Fig. 7 middle), it seems likely that mechanism (3) can be ruled out. However, Stuart et al. (2009) also noted that without information such as unsaturated zone porewater concentrations, distinguishing between the other mechanisms is unlikely to be possible. Existing research in the Chalk (Hampshire (UK) (Sorensen et al., 2015), Northern France (Chen et al., 2019)) has generally shown bypass flow to be a relatively small or insignificant component of total nitrate transport in the unsaturated zone. If the same is true of the time series used in this research, it seems plausible that mechanism (2) can also be ruled out. Further, the requirement in this research to resample nitrate concentrations to monthly mean values means that short term, sub-monthly

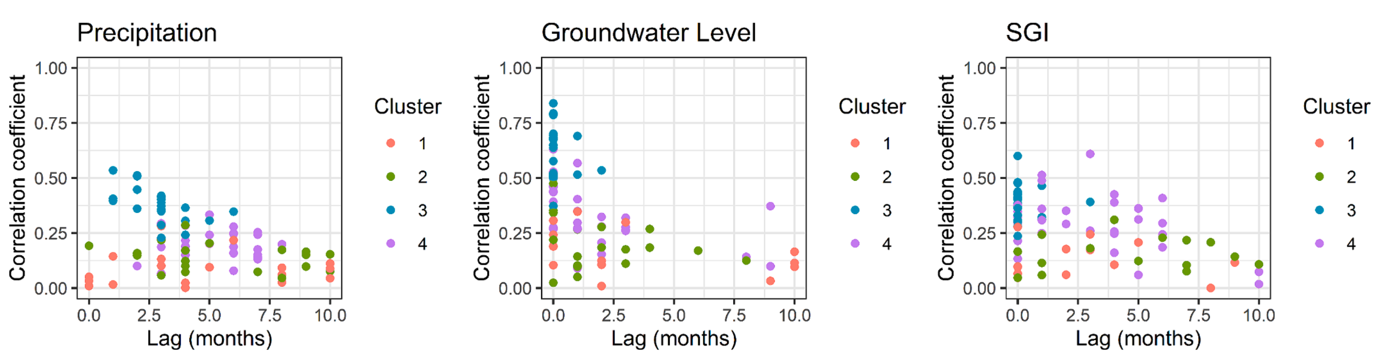

Fig. 7. Maximum correlations and lags between standardised detrended monthly nitrate concentrations and monthly precipitation totals (left), monthly mean groundwater levels (centre), and standardised groundwater level index (SGI, right), split by cluster. Contains data from Hollis et al. (2023) licensed under the Open Government Licence v3.0.

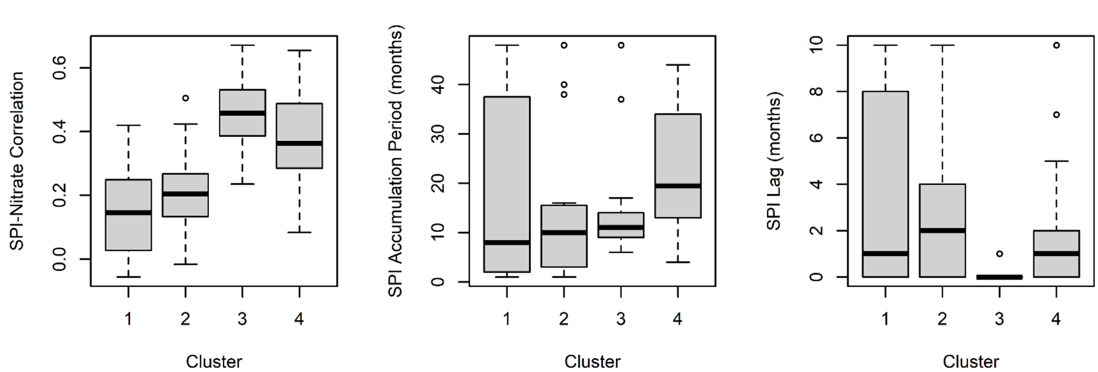

Fig. 8. Boxplots of the maximum correlation coefficients (left), corresponding accumulation period (middle), and lag (right) for Standardised Precipitation Index (SPI)-standardised detrended monthly nitrate concentration correlations. Contains data from Hollis et al. (2023) licensed under the Open Government Licence v3.0.

changes in nitrate that may be associated with bypass flow events may be “smoothed out”. The remaining mechanisms (piston flow and a changing flow path) controlling cluster 3 and 4 behaviour are likely to be linked.

4.2. Implications for nitrate fluctuations in groundwater under future climate and land use change

Climate change projections for the UK show wetter winters and drier summers (Met Office, 2018) and consequently greater seasonal range in groundwater levels (Hannaford et al., 2023). The differences between cluster 3 and 4 and the potential hydrogeological controls on this variability have important implications for how climate change may affect future nitrate fluctuations in groundwater. Piston flow represents a transfer of energy from the land surface to water table. Any impacts of climate change on precipitation and recharge will be near-instantly transferred to the water table. Nitrate fluctuations in groundwater will therefore be principally controlled by legacy N in the unsaturated zone immediately above the water table. Land use change impacts on N leaching will have a lagged impact on nitrate at the water table associated with travel times in the unsaturated zone. In contrast, bypass flow represents the transfer of mass (of nitrate) from the land surface to the water table. In this mechanism, nitrate fluctuations may be due to current land use, and land use change impacts on leaching may affect nitrate at the water table near instantaneously.

Assuming piston flow and changing flow-paths are the dominant mechanisms controlling nitrate fluctuations, a greater seasonal range in precipitation, groundwater recharge and levels would be expected to result in a greater range in nitrate concentrations. For a given series of precipitation events, groundwater levels and nitrate concentrations in cluster 3 may respond more rapidly than cluster 4. In contrast, recovery back to lower nitrate concentrations may be slower in cluster 4 than in cluster 3 as groundwater levels are less flashy in the former.

Under such climate change scenarios, a key factor is the relationship between the change in water level fluctuation and any legacy nitrate peak in the unsaturated zone. Where there is a legacy peak in the unsaturated zone with higher nitrate concentrations in the unsaturated zone porewater than in groundwater, increased seasonality in groundwater levels may result in increased seasonality in groundwater nitrate due to piston flow and changing flow-paths. Conversely, if nitrate concentrations in the unsaturated zone are lower than in groundwater, increased seasonality in groundwater levels may result in shift in phase in the seasonality of nitrate in groundwater (i.e. decreases in nitrate when groundwater levels are higher).

4.3. Limitations and recommendations for further work

There are a number of limitations to the research presented here. Due to a dearth of data for each borehole’s catchment, the potential role of changing land use and nitrate leaching on short term nitrate fluctuations has not been evaluated in this research. This should be considered in future work. It would be beneficial to upscale the approach to the national scale (where groundwater nitrate data are also reported as total oxidised nitrogen (TON)) and potentially internationally. The methodological framework developed could be tested to assess modes of fluctuation in nitrate time series across a wider range of hydrogeological (e.g. different aquifers, unconfined/confined) and hydroclimatic settings. Within our research, the locations of the time series analysed are biased to the Chalk aquifer, and within the Chalk are further biased to public water supply abstractions which are typically located in river valleys. The cluster analysis approach adopted requires monthly data, with missing values imputed by linear interpolation. As such, the methodology cannot reveal processes at a sub-monthly level, such as short term spikes which may be associated with bypass recharge events.

We correlated standardised nitrate time series with groundwater level and SGI time series from observation boreholes which are known to have minimal abstraction influence that are used in hydrological status reporting (Mackay et al., 2015). This approach has benefits as these observation boreholes are likely to be reasonable indicators of groundwater resource status across the aquifers in the study area. However, as well as regional groundwater level status, nitrate time series at pumping boreholes are also likely to be affected by localised pumping-affected groundwater levels. Comparing correlations between groundwater nitrate time series with groundwater levels recorded from regional and local (i.e. affected by pumping) observation boreholes and pumping boreholes may reveal further insights into the processes controlling nitrate fluctuations. Use of a multi-variate statistical modelling approach to explore evidence for interactions between the driving variables used here would also be beneficial.

In this research it has not been possible to infer the exact balance of the different nitrate transport mechanisms for each site. Based on existing literature (Chen et al., 2019; Sorensen et al., 2015), we have had to make assumptions about the dominant processes controlling fluctuations (piston flow and changing flow-paths). Detailed information on porewater nitrate concentrations would be needed on a site-by-site basis to differentiate which processes are most important. Comparing the timescales for changes in precipitation, recharge, and groundwater level seasonality with the time for the legacy nitrate peak in the unsaturated zone to reach the water table would be a useful area to target further work. Another alternative approach to collection of porewater data would be to combine the analysis of nitrate data with a determinand that is non-conservative in the unsaturated zone, such as microbial contaminants using flow cytometry or other methods. Concurrent increases in a non-conservative determinand and nitrate in groundwater may indicate that transport through the unsaturated zone is via rapid bypass flow rather than slower piston flow.

5. Conclusions

This research has analysed a large dataset of time series of nitrate concentrations in groundwater at the regional scale using a combination of cluster analyses and standardised indices for the first time. The following conclusions can be drawn:

- Cluster analysis has revealed different modes of temporal fluctuations in nitrate concentrations. Two clusters show long term increasing and decreasing trends. These may be associated with depth of groundwater flow system intercepted by the boreholes and springs in each cluster.
- Decadal and seasonal changes associated with hydrometeorological variability are present in two clusters, which are weakly spatially coherent across the North and South Downs. Cross-correlation of nitrate time series with groundwater level and precipitation indices show that the extent of nitrate fluctuation appears to be controlled by precipitation and groundwater level fluctuation. This may be due to a combination of piston flow and changing groundwater flow-paths.
- Under future climate change, nitrate fluctuations may change associated with the changing intersection of the water table and the legacy nitrate peak in the unsaturated zone.
- The timescales for land use change impacts on nitrate at the water table will vary substantially depending on the dominant process controlling nitrate fluctuations. Processes which represent a transfer of mass (bypass flow) will impact concentrations much more rapidly than processes representing a transfer of energy (piston flow).

6. Data availability statement

Groundwater nitrate and groundwater level time series are available from the Environment Agency on request and at Open WIMS data (https://environment.data.gov.uk/water-quality/view/landing) and Hydrology Data Explorer – Explore (https://environment.data.gov.uk/hydrology/explore). Precipitation data from HadUK-Grid (Hollis et al.,

2023) are available from https://catalogue.ceda.ac.uk/uuid/b39898e76ab7434a9a20a6dc4ab721f0. All figures contain Environment Agency data licensed under the Open Government Licence v3.0.

CRediT authorship contribution statement

M.J. Ascott: Conceptualization, Formal analysis, Methodology, Investigation, Writing - original draft, Writing - review & editing. **D.C. Gooddy:** Conceptualization, Writing – review & editing. **B. Marchant:** Conceptualization, Writing – review & editing. **N. Kieboom:** Supervision, Conceptualization, Funding acquisition, Writing – review & editing. **H. Bray:** Data curation, Writing – review & editing. **S. Gomes:** Project administration, Funding acquisition, Writing – review & editing.

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.

Acknowledgements

MJA, BM and DCG publish with permission of the Director, British Geological Survey. This research was funded by the Environment Agency of England through the project “Impacts of climate and land use change on groundwater quality”. This work was also supported by the British Geological Survey via NERC national capability and NERC Climate change in the Arctic-North Atlantic region and impact on the UK (CANARI) project (NE/W004984/1).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jhydrol.2024.131052.

References

Abascal, E., Gómez-Coma, L., Ortiz, I., Ortiz, A., 2022. Global diagnosis of nitrate pollution in groundwater and review of removal technologies. Sci. Total Environ. 810, 152233.

Environment Agency, 2019. 2021 River Basin Management Plan, Bristol, UK. https://consult.environment-agency.gov.uk/++preview++/environment-and-business/challenges-and-choices/user_uploads/nitrates-pressure-rbmp-2021.pdf.

Allen, D., Brewerton, L., Coleby, L., Gibbs, B., Lewis, M., MacDonald, A., Wagstaff, S., Williams, A., 1997. The physical properties of major aquifers in England and Wales. UK, British Geological Survey, Keyworth, p. 333.

Ascott, M.J., Wang, L., Stuart, M.E., Ward, R.S., Hart, A., 2016. Quantification of nitrate storage in the vadose (unsaturated) zone: a missing component of terrestrial N budgets. Hydrol. Processes 30 (12), 1903–1915.

Ascott, M.J., Gooddy, D.C., Wang, L., Stuart, M.E., Lewis, M.A., Ward, R.S., Binley, A.M., 2017a. Global patterns of nitrate storage in the vadose zone. Nat. Commun. 8 (1), 1416.

Ascott, M.J., Marchant, B.P., Macdonald, D., McKenzie, A.A., Bloomfield, J.P., 2017b. Improved understanding of spatio-temporal controls on regional scale groundwater flooding using hydrograph analysis and impulse response functions. Hydrol. Processes 31 (25), 4586–4599.

Ascott, M.J., Stuart, M.E., Gooddy, D.C., Marchant, B.P., Talbot, J.C., Surridge, B.W.J., Polya, D.A., 2019. Provenance of drinking water revealed through compliance sampling. Environ. Sci. Processes Impacts 21 (6), 1052–1064.

Ascott, M.J., Macdonald, D.M.J., Black, E., Verhoef, A., Nakohoun, P., Tirogo, J., Sandwidi, W.J.P., Bliefernicht, J., Sorensen, J.P.R., Bossa, A.Y., 2020. In situ observations and lumped parameter model reconstructions reveal intra-annual to multidecadal variability in groundwater levels in sub-saharan Africa. Water Resour. Res. 56 (12), e2020WR028056.

M.J. Ascott Groundwater resources in the UK 2017 http://www.bgs.ac.uk/research/groundwater/waterResources/GroundwaterInUK/home.html.

Bloomfield, J.P., Marchant, B.P., 2013. Analysis of groundwater drought building on the standardised precipitation index approach. Hydrol. Earth Syst. Sci. 17 (12), 4769–4787.

Bloomfield, J., Marchant, B., Bricker, S., Morgan, R., 2015. Regional analysis of groundwater droughts using hydrograph classification. Hydrol. Earth Syst. Sci. 19 (10), 4327–4344.

Bloomfield, J.P., Marchant, B.P., McKenzie, A.A., 2019. Changes in groundwater drought associated with anthropogenic warming. Hydrol. Earth Syst. Sci. 23 (3), 1393–1408.

César, E., Wildemeersch, S., Orban, P., Carrière, S., Brouyère, S., Dassargues, A., 2014. Simulation of spatial and temporal trends in nitrate concentrations at the regional scale in the upper dyle basin. Belgium. Hydrogeology Journal 22 (5), 1087–1100.

Chen, N., Valdes, D., Marlin, C., Blanchoud, H., Guerin, R., Rouelle, M., Ribstein, P., 2019. Water, nitrate and atrazine transfer through the unsaturated zone of the chalk aquifer in northern France. Sci. Total Environ. 652, 927–938.

Dodds, W.K., Bouska, W.W., Eitzmann, J.L., Pilger, T.J., Pitts, K.L., Riley, A.J., Schloesser, J.T., Thornbrugh, D.J., 2009. Eutrophication of U.S. freshwaters: analysis of potential economic damages. Environ. Sci. Technol. 43 (1), 12–19.

Grath, J., Scheidleder, A., Uhlig, S., Weber, K., Kralik, M., Keimel, T., Gruber, D., 2001. The EU water framework directive: statistical aspects of the identification of groundwater pollution trends, and aggregation of monitoring results. Final report, Austrian Federal Ministry of Agriculture and Forestry, Environment and Water Management.

Hannaford, J., Mackay, J.D., Ascott, M., Bell, V.A., Chitson, T., Cole, S., Counsell, C., Durant, M., Jackson, C.R., Kay, A.L., Lane, R.A., Mansour, M., Moore, R., Parry, S., Rudd, A.C., Simpson, M., Facer-Childs, K., Turner, S., Wallbank, J.R., Wells, S., Wilcox, A., 2023. The enhanced future flows and groundwater dataset: development and evaluation of nationally consistent hydrological projections based on UKCP18. Earth Syst. Sci. Data 15 (6), 2391–2415.

Hansen, B., Thorling, L., Dalgaard, T., Erlandsen, M., 2011. Trend reversal of nitrate in danish groundwater - a reflection of agricultural practices and nitrogen surpluses since 1950. Environ. Sci. Technol. 45 (1), 228–234.

Hollis, D., McCarthy, M., Kendon, M., Legg, T., 2023. HadUK-Grid Climate Observations by Administrative Regions over the UK, v1.2.0.ceda (1836-2022). . NERC EDS Centre for Environmental Data Analysis. DOI:https://catalogue.ceda.ac.uk/uuid/b39898e76ab7434a9a20a6dc4ab721f0.

House of Commons Environmental Audit Committee, 2018. UK Progress on Reducing Nitrate Pollution, London, UK.

Hudak, P.F., 2000. Regional trends in nitrate content of Texas groundwater. J. Hydrol. 228 (1), 37–47.

Huebsch, M., Fenton, O., Horan, B., Hennessy, D., Richards, K.G., Jordan, P., Goldscheider, N., Butscher, C., Blum, P., 2014. Mobilisation or dilution? nitrate response of karst springs to high rainfall events. Hydrol. Earth Syst. Sci. 18 (11), 4423–4435.

Jones, H.K., Morris, B., Cheney, C.S., Brewerton, L., Merrin, P.D., Lewis, M.A., MacDonald, A.M., L.M., C., Talbot, J.C., McKenzie, A.A., M.J., B., Cunningham, J.E., Robinson, V., 2000. The physical properties of minor aquifers in England and Wales, British Geological Survey.

Jones, H., Robins, N., 1999. The chalk aquifer of the south downs. British Geological Survey.

Jutglar, K., Hellwig, J., Stoelzle, M., Lange, J., 2021. Post-drought increase in regional-scale groundwater nitrate in Southwest Germany. Hydrol. Processes 35 (8), e14307.

Kawagoshi, Y., Suenaga, Y., Chi, N.L., Hama, T., Ito, H., Duc, L.V., 2019. Understanding nitrate contamination based on the relationship between changes in groundwater levels and changes in water quality with precipitation fluctuations. Sci. Total Environ. 657, 146–153.

Lapworth, D., Boving, T., Brauns, B., Dottridge, J., Hynds, P., Kebede, S., Kreamer, D., Misstear, B., Mukherjee, A., Re, V., Sorensen, J., Vargas, C.R., 2022. Groundwater quality: global challenges, emerging threats and novel approaches. Hydrgeol. J.

Li, X., Li, J., Xi, B., Yuan, Z., Zhu, X., Zhang, X., 2015. Effects of groundwater level variations on the nitrate content of groundwater: a case study in Luoyang area. China. Environmental Earth Sciences 74 (5), 3969–3983.

Mackay, J., Jackson, C., Brookshaw, A., Scaife, A., Cook, J., Ward, R., 2015. Seasonal forecasting of groundwater levels in principal aquifers of the United Kingdom. J. Hydrol. 530, 815–828.

Marchant, B.P., Bloomfield, J.P., 2018. Spatio-temporal modelling of the status of groundwater droughts. J. Hydrol. 564, 397–413.

McAleer, E., Coxon, C., Mellander, P.-E., Grant, J., Richards, K., 2022. Patterns and drivers of groundwater and stream nitrate concentrations in intensively managed agricultural catchments. Water 14 (9), 1388.

McKee, T.B., Doesken, N.J., Kleist, J., 1993. The relationship of drought frequency and duration to time scales. In: Proceedings of the 8th Conference on Applied Climatology. American Meteorological Society Boston, pp. 179–183.

Muniz, D.H.F., Oliveira-Filho, E.C., 2023. Multivariate statistical analysis for water quality assessment: a review of research published between 2001 and 2020. Hydrology 10 (10), 196.

Musacchio, A., Re, V., Mas-Pla, J., Sacchi, E., 2020. EU nitrates directive, from theory to practice: environmental effectiveness and influence of regional governance on its performance. Ambio 49 (2), 504–516.

M. Office UK Climate Projections 2018 https://www.metoffice.gov.uk/research/collaboration/ukcp.

Patel, P.S., Pandya, D.M., Shah, M., 2023. A holistic review on the assessment of groundwater quality using multivariate statistical techniques. Environ. Sci. Pollut. Res. 30 (36), 85046–85070.

Pretty, J.N., Brett, C., Gee, D., Hine, R., Mason, C., Morison, J., Raven, H., Rayment, M., Van der Bijl, G., 2000. An assessment of the total external costs of UK agriculture. Agr. Syst. 65 (2), 113–136.

Prudhomme, C., Hannaford, J., Harrigan, S., Boorman, D., Knight, J., Bell, V., Jackson, C., Svensson, C., Parry, S., Bachiller-Jareno, N., Davies, H., Davis, R., Mackay, J., McKenzie, A., Rudd, A., Smith, K., Bloomfield, J., Ward, R., Jenkins, A., 2017. Hydrological outlook UK: an operational streamflow and groundwater level forecasting system at monthly to seasonal time scales. Hydrol. Sci. J. 62 (16), 2753–2768.

R Core Team, 2022. R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria.

Rangeley-Wilson, C., 2021. Chalk Stream Restoration Strategy, CaBA.
Rivett, M.O., Buss, S.R., Morgan, P., Smith, J.W., Bemment, C.D., 2008. Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. Water Res. 42 (16), 4215–4232.
Roy, S., Speed, C., Bennie, J., Swift, R., Wallace, P., 2007. Identifying the significant factors that influence temporal and spatial trends in nitrate concentrations in the Dorset and Hampshire Basin chalk aquifer of southern England. Q. J. Eng. Geol. Hydrogeol. 40 (4), 377–392.
Rozemeijer, J.C., Broers, H.P., Geer, F.C.V., Bierkens, M.F.P., 2009. Weather-induced temporal variations in nitrate concentrations in shallow groundwater. J. Hydrol. 378 (1), 119–127.
Rupert, M.G., 2008. Decadal-Scale Changes of Nitrate in Ground Water of the United States, 1988–2004. J. Environ. Qual. 37 (S5), S-240–S-248. https://doi.org/10.2134/jeq2007.0055.
Smith, J.T., Clarke, R.T., Bowes, M.J., 2010. Are groundwater nitrate concentrations reaching a turning point in some chalk aquifers? Sci. Total Environ. 408 (20), 4722–4732.
Sorensen, J.P.R., Butcher, A.S., Stuart, M.E., Townsend, B.R., 2015. Nitrate fluctuations at the water table: implications for recharge processes and solute transport in the chalk aquifer. Hydrol. Processes 29 (15), 3355–3367.
Sorensen, J.P.R., Davies, J., Ebrahim, G.Y., Lindle, J., Marchant, B.P., Ascott, M.J., Bloomfield, J.P., Cuthbert, M.O., Holland, M., Jensen, K.H., Shamsudduha, M., Villholth, K.G., MacDonald, A.M., Taylor, R.G., 2021. The influence of groundwater abstraction on interpreting climate controls and extreme recharge events from well hydrographs in semi-arid South Africa. Hydrgeol. J.
Stuart, M., Chilton, P., Kinniburgh, D., Cooper, D., 2007. Screening for long-term trends in groundwater nitrate monitoring data. Q. J. Eng. Geol. Hydrogeol. 40 (4), 361–376.
Stuart, M., Chilton, P.J., Butcher, A.S., 2009. Nitrate fluctuations in groundwater: review of potential mechanisms and application to case studies. British Geological Survey, Nottingham, UK.
Stuart, M.E., Gooddy, D.C., Bloomfield, J.P., Williams, A.T., 2011. A review of the impact of climate change on future nitrate concentrations in groundwater of the UK. Sci. Total Environ. 409 (15), 2859–2873.
Stuart, M.E., Lapworth, D.J., 2016. Macronutrient status of UK groundwater: nitrogen, phosphorus and organic carbon. Sci. Total Environ. 572, 1543–1560.
Svensson, C., Hannaford, J., Prosdocimi, I., 2017. Statistical distributions for monthly aggregations of precipitation and streamflow in drought indicator applications. Water Resour. Res. 53 (2), 999–1018.
Van Meter, K.J., Van Cappellen, P., Basu, N.B., 2018. Legacy nitrogen may prevent achievement of water quality goals in the Gulf of Mexico. Science.
Vicente-Serrano, S.M., Beguería, S., López-Moreno, J.I., 2010. A multiscalar drought index sensitive to global warming: the standardized precipitation evapotranspiration index. J. Clim. 23 (7), 1696–1718.
Wang, L., Stuart, M.E., Lewis, M.A., Ward, R.S., Skirvin, D., Naden, P.S., Collins, A.L., Ascott, M.J., 2016. The changing trend in nitrate concentrations in major aquifers due to historical nitrate loading from agricultural land across England and Wales from 1925 to 2150. Sci. Total Environ. 542, 694–705.
Webster, R., Oliver, M.A., 1990. Statistical methods in soil and land resource survey. Oxford University Press (OUP).
World Meteorological Organization, 2017. WMO guidelines on the calculation of climate normals. Switzerland, Geneva.
Zanotti, C., Rotiroti, M., Redaelli, A., Caschetto, M., Fumagalli, L., Stano, C., Sartirana, D., Bonomi, T., 2023. Multivariate time series clustering of groundwater quality data to develop data-driven monitoring strategies in a historically contaminated urban area. Water 15 (1), 148.