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Removal of previously planted tree and shrub species and the impacts on the shallow groundwater chemistry of coastal dune systems in northern Ireland

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ABSTRACT

Nitrogen (N) input to naturally oligotrophic dune systems is a global issue. This study assessed the groundwater nitrogen impact of growing sea buckthorn, sea buckthorn and tree removal, a golf course and a small stream on two coastal sand dune systems over several years. Groundwater nitrogen concentrations were monitored at both sites, during and after the removal of previously planted species. Sea buckthorn and Corsican Pine were removed in a single season from site one, however a series of sea buckthorn removal events occurred at site two over a 4 year period. Sea buckthorn was pulled up with the roots and burnt at site, but the tree roots were left in the ground. Concentrations of NO_3-N and total N from shallow piezometers and eluted sand samples were assessed against pre-defined criteria which treat N as a groundwater contaminant in coastal dune systems. It was found that neither the management of the golf course at the first site, or the removal of the Corsican pines at the second increased groundwater nitrogen above the 'level of concern', set at <0.2 mg/l N. Growing sea buckthorn was seen to cause 'possible contamination' in groundwater (between 0.2 and 1 mg/l N). Sea buckthorn removal increased the groundwater NO_3-N concentrations above the Threshold Value of 3 mg/l NO_3-N and subsequent attenuation of groundwater nitrogen concentrations to 'below concern' took <5 years. Dual nitrate isotopes provided strong evidence for denitrification as the primary reason for this decrease in concentration.

1. Introduction

The uniqueness of coastal sand dune systems is due to their formation, naturally dynamic behaviour and as a habitat for many species of flora and fauna adapted to specific habitats within the system. Dune systems are rainwater fed and some UK coastal dunes systems are thought to be freshwater aquifers on top of impermeable bedrock or superficial deposits with no saline intrusion (Stratford et al., 2013). Groundwater is seen to dome in the dunes acting to stabilize dunes as saturated sand is more resistant to aeolian deflation (Stratford et al., 2013, 2014). The humid depressions and ephemeral ponds that occur in dune slacks support native flora and fauna dependent on seasonal groundwater flooding (Ranwell, 1960) and low nutrient groundwater. The extent of these naturally oligotrophic coastal dune systems are currently in decline (Jones et al., 2006; Pye et al., 2014) and additional nutrient input is a threat to the habitats (Davy et al., 2006; Rhymes et al., 2014; Whiteman et al., 2010).

Anthropogenic stress on dune habitats is increasing globally. Coastal dunes and the ecosystems they support are at risk from many factors including climate change (Clarke and Sanitwong Na Ayutthaya, 2010; Curreli et al., 2013), excess nutrient loadings (Bobbink et al., 2022; Davy et al., 2010; Jones et al., 2006; Rhymes et al., 2014, 2015; Whiteman et al., 2017), changing management techniques (van der Meulen and Salman, 1996), irreversible decalcification and acidification (Sival et al., 1997), and salinisation (Stuyfzand, 2016).

Excess nutrients from dry or wet deposition from agricultural land,

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land/dune management and surface water has been seen to perturb the oligotrophic dune ecosystems stressing species adapted to these conditions (Rhymes et al., 2014). Excess nutrients will increase the dominance of nutrient-demanding species, causing an additional loss of diversity and key species (Bobbink et al., 2015, 2022; Davy et al., 2010; Jones et al., 2006). Guidelines from the UK Environment Agency (Davy et al., 2010) suggest concentration of total inorganic nitrogen of dune groundwater should be < 0.20 mg/l N, concentrations between 0.20 and 0.40 N mg/l N may indicate contamination, and >1.0 N mg/l N indicate likely contamination and merit concern. Additionally, Rhymes et al. (2014) showed a change in plant species composition, with an increase in nitrophilous species at around 0.2 mg/l dissolved inorganic nitrogen. As most N is from nitrate, work by Whiteman et al. (2017) produced a threshold value (TV) of 3 mg/l NO_3-N for dune groundwaters.

Sea buckthorn (*Hippophae rhamnoides*) is a non-native deciduous shrub with narrow leaves often planted in coastal sand dunes to limit sand erosion (Binggeli et al., 1992). It is well suited to the calcareous, nutrient poor coastal dune habitat (Pearson and Rogers, 1962). Sea Buckthorn is an actinorhizal plant with a symbiotic relationship with the *Frankia* bacteria, a nitrogen-fixing, nodule forming endophyte (Kato et al., 2007), which assimilates nitrate in its leaves and stems (Troelstra et al., 1987). Nitrogen fixation in the root nodules is the main pathway for nitrogen cycling in sea buckthorn (Liu et al., 2024) and elevates soil nitrogen concentration (Binggeli et al., 1992; Jones et al., 2006; Pearson and Rogers, 1962; Stuyfzand, 1993). Using lysimeter data, Stuyfzand (1993) estimated that 300–500 μmol N m^{-2} d^{-1} of nitrogen was fixed by sea buckthorn roots making it an important source of nitrate in dune groundwaters. Increase in soil organic matter and soil nitrogen has been linked to sea buckthorn leaf litter (Isermann et al., 2007).

Sea buckthorn is a habitat and food source for local wildlife and removal has to take this into consideration. However, it can dominate dune flora (Pearson and Rogers, 1962), change the species composition, and decrease species richness and diversity with plant density (Isermann, 2008; Isermann et al., 2007). It competes with low-growing species (Pearson and Rogers, 1962) and produces nitrate causing a problem for native, low growing and oligotrophic dunes species. Sea buckthorn has been actively managed by removal at North Bull Island, Ireland, as it is a potential threat to fauna, flora and groundwater level (Harris and Council, 2014), even though it was found to be used by a small number of bird species for feeding and nesting (Cooney, 2019).

Returning a more natural flora and fauna to the dune systems is beneficial globally and is helped by the removal of planted species that are often not suited to the dune environment or non-native. The removal of large species also reduces evapotranspiration, potentially raising groundwater levels leading to more ephemeral ponds which may allow more natural vegetation to colonise in its place. Minimally disturbed land with an indigenous vegetation generally yields good water quality, however if the land is disturbed by, for example removing planted species, water quality is impacted due to mobilization of nutrients and fine sediments (Davies-Colley, 2013).

This study monitored the effect on groundwater quality and groundwater level over several years during the removal of sea buckthorn at the dune systems at Portstewart and Magilligan Umbra and the felling of a stand of Corsican pines at the latter. The aims of the study were 1) monitor the impact of removal on the shallow groundwater nitrogen budget; 2) monitor the effect of a coastal dune golf course on the groundwater nitrogen budget at Portstewart; 3) assess the impact of the Umbra Burn on the Magilligan Umbra groundwater nitrogen budget; 4) assess the concentration of nitrate and nitrite within the unsaturated zone. This study uses a variety of techniques to quantify the effects of removal of sea buckthorn and Corsican Pine on water quality in situ and additionally the impact of a golf course on groundwater nitrate concentrations. The singular removal at Magilligan Umbra allowed the impact of removal to be seen with no further disturbance whereas the phased removal at Portstewart showed the effect of disturbances from multiple removals. The study concentrated on shallow groundwater as this is more likely to be available for plant species, however the deeper groundwater system was assessed at Magilligan Umbra.

2. Methods

2.1. Study area

Portstewart sand dunes, Northern Ireland, are part of the Bann Estuary Special Area of Conservation (SAC) for fixed dunes with herbaceous vegetation (grey dunes 98.5 ha), embryonic shifting dunes (0.6 ha) and shifting dunes along the shoreline with *Ammophila arenaria* (white dunes 2.9 ha), they are also an Area of Special Scientific Interest (DOE and Environment, 2015) (Fig. 1). The northern boundary of the dune system is the North Atlantic Ocean and the southern and western boundaries are the River Bann (Fig. 1b). The eastern part of the dune system contains a golf course. Groundwater discharges to the Bann estuary and the North Atlantic Ocean (Fig. 1b).

Sea buckthorn was planted in the early 1900's to stabilize parts of the Portstewart dune system, but has since become invasive (Binggeli et al., 1992; DOE and Environment, 2015; McKeown, 2015a); the management and removal is part of the SAC conservation objectives 2015 (McKeown, 2015a). The different phases of Sea Buckthorn removal at Portstewart were catalogued from aerial photographs to produce Fig. 1b.

The Magilligan Umbra dunes, Northern Ireland (Fig. 1), are part of the larger Magilligan SAC (McKeown, 2015b) and ASSI managed by Ulster Wildlife. The SAC conservation objectives (McKeown, 2015b) highlight the effect on groundwater levels of increasing rankness towards scrub and the presence of sea buckthorn. Suggested management included increased grazing, removal of scrub, Corsican pine and sea buckthorn (McKeown, 2015b). Magilligan Umbra is an approximately 640 m wide and 1000 m long section of the much larger Magilligan dune system of approximately 800 ha (Robins and Wilson, 2017). It is bounded to the north by the beach and North Atlantic Ocean, to the south by basalt and limestone cliffs, and to the east and west by further sand dunes. To the west there is a holiday complex within the dunes. The Magilligan Umbra Burn runs the whole length of the system below the cliffs and behind the road and rail track (Fig. 1c). Lower Jurassic mudstone intruded by the Magilligan Sill underlies the dunes with glacial deposits possibly occurring between the bedrock and sand deposits. Groundwater flow below Magilligan Umbra is NNE towards the beach and sea (Fig. 1c).

A network of shallow piezometers was installed at both Magilligan Umbra and Portstewart coastal dune systems to monitor the groundwaters chemical and level response to the vegetation removal and subsequent soil disturbance. At both sites, sea buckthorn was ripped out with the roots and burnt on site; regrowth was pulled up or chemically treated. The Corsican pines were felled at Magilligan Umbra, but the ground and the roots were left undisturbed. The study also monitored the impact of Portstewart golf course management on groundwater nitrogen. Multiple techniques were used to investigate the change in groundwater nitrogen (and specifically nitrate) within the system down flow of the sea buckthorn removal areas and away from their influence to provide a causal link.

2.2. Piezometer network

Piezometers were emplaced by hand augering an initial pilot hole followed by driving with a steel rod and sledgehammer until the rest water level was 0.5 m above the top of the piezometer tip. The casing was cut just below the ground surface and a rubber well cap plug installed from which water level loggers could be suspended. All piezometers were installed in dune slacks. Piezometers MUP1 to MUP16 (Magilligan Umbra Fig. 1c) and PS1 to PS22 (Portstewart Fig. 1b) comprise a galvanised steel Casagrande piezometer point (500 mm length) with an internal porous membrane connected to a uPVC solid casing. Piezometers MUP1 to MUP16 were installed at Magilligan

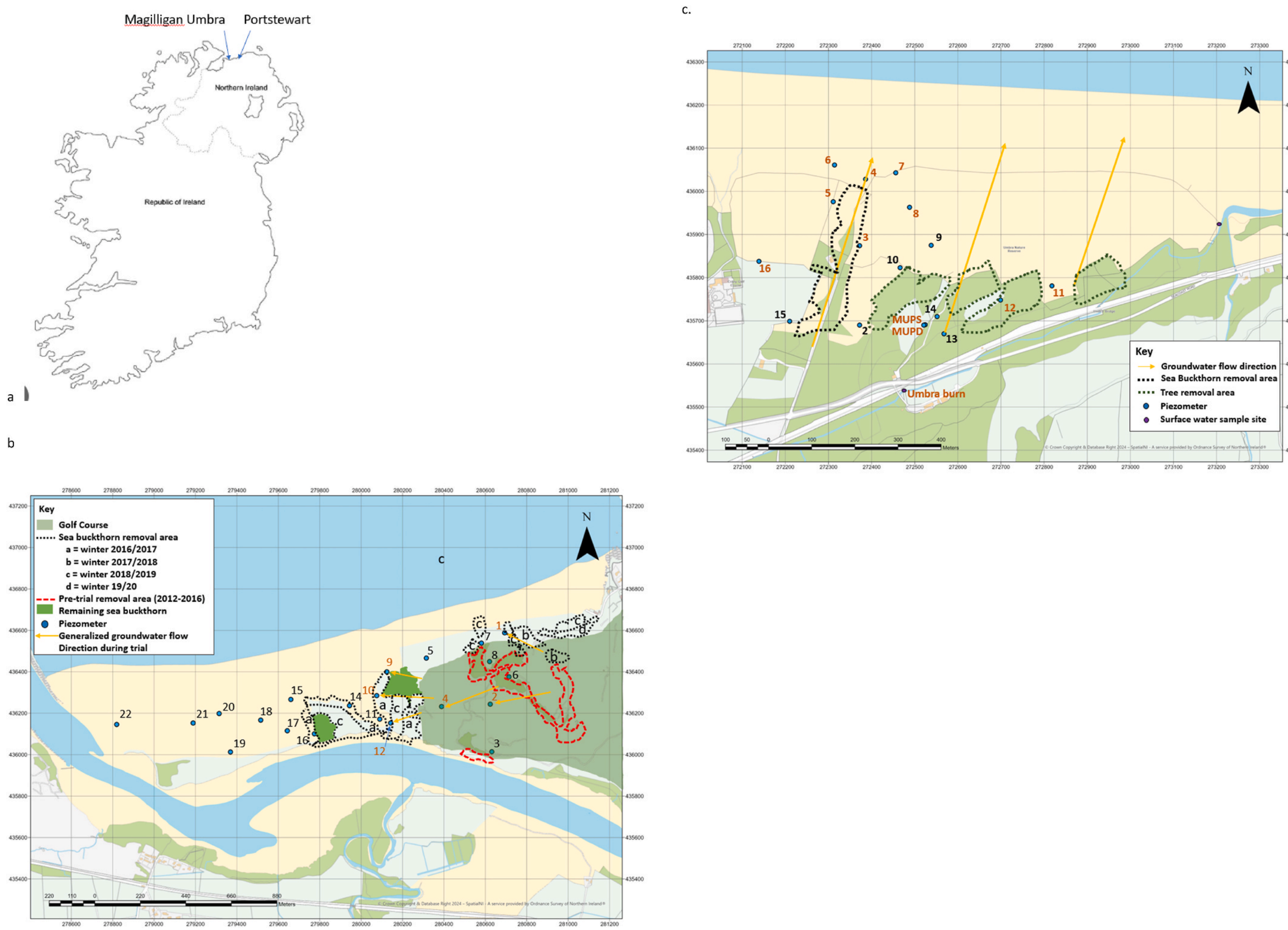

Fig. 1. a) The island of Ireland with the location of the Portstewart and Magilligan Umbra sites highlighted b) the Portstewart site c) Magilligan Umbra site. Sampled sites are highlighted with brown numbering. Co-ordinates shown are Irish Grid Reference. This Intellectual Property is based upon Crown copyright material and is reproduced with the permission of Land & Property Services under Delegated Authority from the Keeper of Public Records, © Crown copyright and database right 2024.

Umbra in September, October and December 2017 to a depth of between 1.27 m and 2.26 m. With an installed diameter of 36 mm for MUP1 to MUP14 and 19 mm for MUP15 and 16 (Fig. 1c). Piezometers PS1 to PS22 were installed at Portstewart in August 2016 to a depth of between 1.07 m and 2.96 m (Fig. 1b) with an installed diameter of 36 mm.

In February 2020 two deeper piezometers were installed at Magilligan Umbra with a power auger using a lost cone method to a depth of 4.5 m (MUPS) and 6.5 m (MUPD). The construction consisted of solid casing with the last 1 m slotted with a geotextile wrap.

Prior to every groundwater sampling round, water levels were measured using a Solinst mini dipper. The measurement datum was the top of the piezometer casing, this was levelled in using a dGPS.

2.3. Groundwater and surface water sampling

Groundwater sampling at Portstewart started in December 2016 during a sea buckthorn removal event (Fig. 1b–Table S1). Sites sampled were a north-south transect through a large area of sea buckthorn where removal had started (PS9, PS10, PS12), the golf course (PS2 and PS4) and PS1 in the north-east (Table 1 and S1). Over time this was refined to increase the cost effectiveness of the trial.

Groundwater sampling at Magilligan Umbra started in January 2018 after the removal of sea buckthorn and the felling of the trees between December 2017 and January 2018 (Tables 1 and 2). Sites sampled included those closely surrounding the sea buckthorn removal area (MUP3, MUP4, MUP6, MUP7), sites within the tree felling area (MUP11 and MUP12), a site down gradient of the tree felling area (MUP8), a site within a putting green (MUP16) and surface water samples from the Umbra Burn (Gauge 1). The deeper piezometers MUPS and MUPD were sampled after installation in March 2021. Over time sampling points were refined to MUP3, MUP4, MUP8, MUP12, MUPS and MUPD. A full sampling grid for both sites can be found in the supplementary material (Table S1).

The groundwater within piezometers at Magilligan Umbra and Portstewart (Fig. 1) were sampled using a Solinst® 410 peristaltic pump, Pt cured Si tubing and rigid PE extension tubing. Shallow piezometers underwent low-flow purging so that the piezometer could recharge during pumping, the two deeper piezometers at Magilligan Umbra were high-flow purged. Surface water from the Umbra Burn was pumped using the same method with the input tubing held above the bed of the stream.

Where a continuous stream of water was possible the sample was pumped through a flow-through cell containing Eh, pH and DO electrodes; SEC (at 25 °C) and temperature were measured outside the flow-through cell. Where a continuous flow was not possible the pH, SEC and a temperature sensor were immersed in a beaker of flowing sample; the beaker was emptied and was allowed to refill prior to measurements being taken. Groundwater was sampled when parameters stabilized. The surface expression of groundwater at Magilligan Umbra was sampled directly from the flooded slack with pH, SEC and temperature sensors

Table 1
Maximum, minimum and seasonal average unsaturated zone depth during the trial for a) Magilligan Umbra and b) Portstewart. Data includes mean unsaturated zone depth during the summer and winter. Note: a negative value indicates the level of groundwater flooding above ground level. Data from manual dip data measured prior to sampling. Elevation of the piezometer top is measured in meters above OD (m aOD) and groundwater level is measured in meters below ground level (m bgl). Contains GSNI data © Crown copyright and database rights.

Piezometer	Elevation	Groundwater level (m bgl)			
	(m aOD)	Total max	Total min	Winter mean	Summer mean
Portstewart					
PS1	2.44	0.97	0.23	0.52	0.81
PS2	2.18	0.94	0.21	0.49	0.76
PS3	2.52	1.84	1.34	1.50	1.67
PS4	1.67	0.82	0.21	0.44	0.72
PS5	2.08	1.26	0.69	0.90	1.19
PS6	3.05	1.40	0.55	0.92	1.13
PS7	1.88	0.65	0.06	0.28	0.50
PS8	2.39	1.00	0.29	0.56	0.81
PS9	1.80	1.25	0.73	0.86	1.16
PS10	2.19	1.63	1.12	1.29	1.54
PS11	1.59	1.17	0.81	0.89	1.06
PS12	1.98	1.63	1.25	1.36	1.52
PS14	1.73	1.27	0.84	0.96	1.21
PS15	1.54	1.25	0.77	0.88	1.17
PS16	0.89	0.77	0.24	0.51	0.60
PS17	1.43	1.13	0.69	0.85	1.03
PS18	1.54	1.06	0.54	0.68	0.99
PS19	1.29	0.71	0.07	0.26	0.61
PS20	1.44	0.80	0.15	0.35	0.73
PS21	1.61	0.96	0.30	0.51	0.89
PS22	2.44	2.15	0.95	1.74	1.86
Magilligan Umbra					
MUP2	2.96	0.72	−0.27	−0.03	0.50
MUP3	3.19	1.24	0.45	0.64	1.03
MUP4	2.42	1.01	0.30	0.53	0.91
MUP5	2.38	0.75	−0.01	0.22	0.58
MUP6	2.55	1.09	0.43	0.61	1.02
MUP7	2.88	1.39	0.70	0.90	1.31
MUP8	2.19	0.62	−0.12	0.09	0.49
MUP9	2.95	0.96	0.18	0.48	0.86
MUP10	2.71	0.59	−0.14	0.11	0.42
MUP11	2.87	0.87	0.32	0.55	0.81
MUP12	2.61	0.45	−0.15	0.04	0.39
MUP13	2.60	0.35	−0.29	−0.06	0.25
MUP14	2.79	0.50	−0.08	0.08	0.47
MUP15	3.00	0.73	−0.04	0.12	0.56
MUP16	3.15	1.08	0.25	0.43	0.87
MUPD	3.88	1.68	1.04	1.09	1.61
MUPS	3.98	1.77	1.14	1.19	1.71

immersed within a beaker in the flood waters.

Bicarbonate was measured on site using a HACH digital titrator, bromocresol green indicator and 1.6 N sulphuric acid. Due to occasional groundwaters colouration, some of the bicarbonate concentrations were checked in the laboratory. All groundwaters and surface waters were analysed for major and minor ions and ammonium. Nitrate isotope ($\delta^{18}O$ - NO_3, $\delta^{15}N$ - NO_3) analysis occurred on selected samples. All water samples were filtered through 0.45 μm cellulose nitrate filters at site into Nalgene LDPE bottles. A subsample was preserved to 0.5% hydrochloric acid and 1% nitric acid for analysis by ICP MS. The major and minor ions were analysed by IC and ICP MS at the BGS laboratories in Keyworth and the ammonium analysis was done by colorimetry at the UKCEH Wallingford laboratory. Isotope preparation and analysis were carried out at the National Environmental Isotope Facility at Keyworth where nitrate was separated on anion resins and prepared as silver nitrate using the method of Silva et al. (2000).

2.4. Sand sampling

To gauge the concentration of nitrate in the interstitial waters of the unsaturated sands, four sand samples were hand augered in different locations at both sites in 2018. Sample 1 was taken at Portstewart at the edge of a recently cleared area of sea buckthorn next to the roots of still standing plants. Sample 2, the control, was augered from an area away from sea buckthorn at Portstewart. Sample 3 was augered from the removal site at Magilligan Umbra and sample 4 was taken from the centre of a stand of sea buckthorn at Portstewart.

The sand samples were recovered from between approximately 280 mm and 500 mm below ground level and were transferred to a 500 ml LDPE Nalgene bottle. The samples were transported back to the BGS's Wallingford laboratory where they were mixed 1:1 with ultrapure water (≥18 Ω), shaken, left overnight and then centrifuged at 14,000 rpm before being filtered with a 0.45 μm cellulose nitrate filter into LDPE Nalgene bottles.

The elutions were analysed for major and minor ions, with the results multiplied by a factor of 2 to account for dilution. A sub sample of the elution from the sea buckthorn impacted area was analysed for $\delta^{18}O$ - NO_3 and $\delta^{15}N$ - NO_3.

3. Results

3.1. Water levels and precipitation

The groundwater water level and precipitation data is described fully in Wilson et al. (2022); below is a short summary. During the period of monitoring from 2016 to 2022, the average precipitation was 991 mm/a. The average precipitation during the typical main groundwater recharge period from September to March was 620 mm/a with a slight increasing trend during the period of monitoring.

April to June typically had less precipitation than any other quarter, with an average of 174.2 mm compared to the average quarterly rainfall of 247.8 mm. July and August were typically characterised by dry conditions interspersed with high intensity rainfall events.

Groundwater levels at Magilligan Umbra and Portstewart follow a sinusoidal pattern of rising during the autumn – winter recharge period (September to March) followed by a decline during the spring – summer discharge period (March to August). High intensity rainfall events in the spring summer period resulted in groundwater levels rising or remaining level.

The variation in unsaturated zone thickness, calculated using manual dip data at the time of groundwater sampling, is marked during summer (sampling events in June to September) and winter (December, January to March) at both dune systems (Table 1).

3.2. Water chemistry

Table 2. Concentration of NO_3-N, NO_2-N, NH_4-N for each sample assessed using guidelines of Davy et al. (2010) and the threshold value of Whiteman et al., (2017). a) Portstewart piezometers. b) Magilligan Umbra. Note: the concentrations given for the sand samples are after correction for elution. PS indicated sample taken at Portstewart, MU indicates sample taken a Magilligan Umbra, n/s indicated no sample taken, samples 'SW nr 12' are samples taken from groundwater flooding around MUP12. The eluted sand samples are not assessed against the guidelines.

Concentrations of NO_3-N, nitrite-N and ammonium-N from groundwater and eluted sand samples are tabulated in Table 2 and compared with the guidelines of Davy et al. (2010) and the threshold value of Whiteman et al. (2017) to help assess the impact of removal over time. The eluted sands and surface waters are contained in the table but were not compared to the groundwater guidelines. The eluted sand samples from the unsaturated zone at Portstewart and Magilligan Umbra show an elevated concentration of NO_3-N below the sites with mature sea

Table 2a

Site	Date	NO_3-N	NO_2-N	NH_4-N	Total N	no concern	possible contamination	cause for concern	above TV
		mg/l	mg/l	mg/l	mg/l	<0.2 mg/l N	0.2–1 mg/l N	>1 mg/l N	>3 mg/l NO_3-N
Groundwater									
PS1	01/12/2016	5.63	0.009	0.010	5.65			✓	✓
PS1	29/01/2018	0.51	<DL	0.005	0.515		✓		
PS1	01/06/2018	0.89	<DL	0.002	0.892		✓		
PS1	09/10/2018	2.56	<DL	0.106	2.67			✓	
PS1	04/02/2019	4.28	<DL	<DL	4.28			✓	✓
PS1	25/06/2019	2.53	0.012	0.016	2.56			✓	
PS1	29/10/2019	4.22	<DL	0.018	4.24			✓	✓
PS1	04/02/2020	3.50	<DL	0.001	3.50			✓	✓
PS1	21/08/2020	8.23	0.075	0.010	8.32			✓	✓
PS1	25/03/2021	2.31	<DL	0.012	2.32			✓	
PS1	30/07/2021	3.19	0.011	<DL	3.20			✓	✓
PS1	11/02/2022	2.79	<DL	0.002	2.79			✓	
PS1	30/01/2023	1.56	<DL	0.025	1.58			✓	
PS2	01/12/2016	0.06	<DL	0.012	0.072	✓			
PS2	30/01/2018	<DL	<DL	0.004	0.004	✓			
PS2	01/06/2018	<DL	<DL	<DL	<DL	✓			
PS2	08/10/2018	<DL	<DL	0.009	0.009	✓			
PS2	04/02/2019	<DL	<DL	<DL	<DL	✓			
PS2	24/06/2019	<DL	<DL	<DL	<DL	✓			
PS2	29/10/2019	0.06	<DL	<DL	0.060	✓			
PS2	04/02/2020	<DL	<DL	0.002	0.002	✓			
PS2	21/08/2020	0.016	<DL	0.014	0.030	✓			
PS2	24/03/2021	<DL	<DL	0.012	0.012	✓			
PS2	30/07/2021	<DL	<DL	<DL	<DL	✓			
PS2	11/02/2022	0.024	<DL	0.002	0.026	✓			
PS2	09/08/2022	<DL	<DL	<DL	<DL	✓			
PS2	30/01/2023	<DL	<DL	0.019	0.019	✓			
PS4	01/12/2016	0.04	<DL	0.011	0.051	✓			
PS4	30/01/2018	<DL	<DL	0.004	0.004	✓			
PS4	04/02/2019	0.02	<DL	<DL	0.020	✓			
PS4	24/06/2019	<DL	<DL	0.064	0.064	✓			
PS4	28/10/2019	<DL	<DL	0.013	0.013	✓			
PS4	04/02/2020	<DL	<DL	0.003	0.003	✓			
PS9	01/12/2016	0.39	<DL	0.003	0.393		✓		
PS9	29/01/2018	0.21	<DL	0.004	0.214		✓		
PS9	05/02/2019	0.21	<DL	<DL	0.210		✓		
PS9	24/06/2019	0.04	<DL	0.030	0.070	✓			
PS9	28/10/2019	0.99	<DL	<DL	0.991		✓		
PS9	03/02/2020	0.51	<DL	0.003	0.508		✓		
PS10	01/12/2016	8.30	<DL	0.015	8.32			✓	✓
PS10	29/01/2018	4.50	<DL	0.015	4.52			✓	✓
PS10	01/06/2018	4.76	<DL	0.003	4.76			✓	✓
PS10	09/10/2018	2.88	<DL	0.005	2.89			✓	
PS10	05/02/2019	3.61	<DL	<DL	3.61			✓	✓
PS10	24/06/2019	7.65	<DL	0.014	7.66			✓	✓
PS10	28/10/2019	2.81	<DL	<DL	2.81			✓	
PS10	03/02/2020	5.05	<DL	0.002	5.05			✓	✓
PS10	21/08/2020	2.98	<DL	0.008	2.99			✓	
PS10	22/03/2021	0.94	<DL	0.012	0.952		✓		
PS10	30/07/2021	1.64	<DL	<DL	1.64			✓	
PS10	11/02/2022	7.21	<DL	0.004	7.22			✓	✓
PS10	09/08/2022	2.97	<DL	<DL	2.97			✓	
PS10	30/01/2023	1.54	0.002	0.019	1.56			✓	
PS12	01/12/2016	3.66	<DL	0.012	3.67			✓	✓
PS12	29/01/2018	3.65	0.009	0.008	3.67			✓	✓
PS12	01/06/2018	1.19	<DL	0.002	1.19			✓	
PS12	09/10/2018	4.90	<DL	0.023	4.92			✓	✓
PS12	05/02/2019	11.46	0.015	<DL	11.5			✓	✓
PS12	25/06/2019	4.84	0.009	<DL	4.85			✓	✓
PS12	29/10/2019	4.94	<DL	0.008	4.95			✓	✓
PS12	03/02/2020	7.69	0.034	0.008	7.73			✓	✓
PS12	21/08/2020	1.31	0.002	0.008	1.32			✓	
PS12	23/03/2021	0.350	<DL	0.011	0.361		✓		
PS12	30/07/2021	0.64	<DL	<DL	0.639		✓		
PS12	11/02/2022	0.487	<DL	0.003	0.490		✓		
PS12	09/08/2022	0.703	0.005	<DL	0.709		✓		
PS12	30/01/2023	0.438	<DL	0.019	0.458		✓		

Table 2b

Site	Date	NO_3-N	NO_2-N	NH_4-N	Total N	no concern	possible contamination	cause for concern	above TV
		mg/l	mg/l	mg/l	mg/l	<0.2 mg/l N	0.2–1 mg/l N	>1 mg/l N	3 mg/l NO_3-N
Groundwater									
MUP3	30/01/2018	0.290	<DL	0.008	0.298		✓		
MUP3	01/06/2018	0.172	<DL	0.019	0.191	✓			
MUP3	10/10/2018	0.286	<DL	0.007	0.293		✓		
MUP3	07/02/2019	0.090	<DL	<DL	0.090	✓			
MUP3	26/06/2019	0.117	<DL	<DL	0.117	✓			
MUP3	30/10/2019	0.138	<DL	0.016	0.154	✓			
MUP3	06/02/2020	0.079	<DL	0.002	0.080	✓			
MUP3	17/08/2020	0.166	<DL	0.006	0.172	✓			
MUP3	19/03/2021	0.015	<DL	0.016	0.031	✓			
MUP3	02/08/2021	0.230	<DL	<DL	0.230		✓		
MUP3	09/02/2022	0.050	<DL	0.002	0.052	✓			
MUP3	11/08/2022	0.159	<DL	<DL	0.159	✓			
MUP3	27/01/2023	0.035	<DL	0.019	0.055	✓			
MUP4	31/01/2018	3.950	<DL	0.005	3.96			✓	✓
MUP4	10/10/2018	14.53	0.074	0.018	14.6			✓	✓
MUP4	06/02/2019	8.800	<DL	<DL	8.80			✓	✓
MUP4	26/06/2019	7.670	<DL	0.009	7.68			✓	✓
MUP4	30/10/2019	5.090	<DL	0.011	5.10			✓	✓
MUP4	06/02/2020	1.448	<DL	0.002	1.45			✓	
MUP4	17/08/2020	0.762	0.003	0.009	0.773		✓		
MUP4	19/03/2021	0.598	<DL	0.011	0.609		✓		
MUP4	02/08/2021	0.180	<DL	<DL	0.180	✓			
MUP4	09/02/2022	0.036	<DL	0.002	0.039	✓			
MUP4	11/08/2022	1.374	0.007	<DL	1.38			✓	
MUP4	27/01/2023	0.020	<DL	0.029	0.049	✓			
MUP5	01/06/2018	0.209	<DL	<DL	0.209		✓		
MUP5	10/10/2018	0.332	<DL	0.007	0.339		✓		
MUP5	06/02/2019	0.186	<DL	<DL	0.186	✓			
MUP5	26/06/2019	0.723	0.004	<DL	0.727		✓		
MUP5	31/10/2019	0.165	<DL	0.023	0.188	✓			
MUP5	06/02/2020	0.114	<DL	0.081	0.195	✓			
MUP6	01/02/2018	0.251	<DL	0.004	0.255		✓		
MUP6	01/06/2018	0.466	<DL	<DL	0.466		✓		
MUP6	10/10/2018	0.153	<DL	0.011	0.164	✓			
MUP6	06/02/2019	0.458	<DL	<DL	0.458		✓		
MUP6	26/06/2019	0.784	<DL	<DL	0.784		✓		
MUP6	30/10/2019	0.361	<DL	<DL	0.361		✓		
MUP6	06/02/2020	0.364	<DL	0.003	0.367		✓		
MUP7	31/01/2018	0.037	<DL	0.006	0.043	✓			
MUP8	13/06/2018	<DL	<DL	0.286	0.286		✓		
MUP8	11/10/2018	0.124	<DL	0.266	0.390		✓		
MUP8	07/02/2019	0.040	<DL	0.202	0.242		✓		
MUP8	26/06/2019	0.054	<DL	0.100	0.154	✓			
MUP8	31/10/2019	<DL	<DL	0.099	0.099	✓			
MUP8	05/02/2020	<DL	<DL	0.073	0.073	✓			
MUP8	17/08/2020	0.009	<DL	0.092	0.128	✓			
MUP8	02/08/2021	1.226	0.120	0.711	2.06			✓	
MUP8	09/02/2022	<DL	<DL	0.122	0.122	✓			
MUP8	11/08/2022	<DL	<DL	0.053	0.053	✓			
MUP11	01/02/2018	<DL	<DL	0.010	0.010	✓			
MUP11	01/06/2018	0.096	<DL	0.016	0.112	✓			
MUP12	01/06/2018	0.070	<DL	0.027	0.097	✓			
MUP12	10/10/2018	<DL	<DL	0.027	0.027	✓			
MUP12	07/02/2019	<DL	<DL	0.054	0.054	✓			
MUP12	27/06/2019	<DL	<DL	0.037	0.037	✓			
MUP12	30/10/2019	<DL	<DL	0.035	0.035	✓			
MUP12	05/02/2020	<DL	<DL	0.049	0.049	✓			
MUP12	17/08/2020	<DL	<DL	0.016	0.016	✓			
MUP12	02/08/2021	<DL	<DL	0.026	0.026	✓			
MUP12	09/02/2022	<DL	<DL	0.019	0.019	✓			
MUP12	11/08/2022	<DL	<DL	<DL	<DL	✓			
MUP12	27/01/2023	0.021	<DL	0.029	0.049	✓			
MUP16	31/01/2018	<DL	<DL	0.022	0.022	✓			
MUP16	11/10/2018	<DL	<DL	0.046	0.046	✓			
Deeper piezometers									
MUPD	19/03/2021	0.602	<DL	0.014	0.616		✓		
MUPD	02/08/2021	0.635	<DL	<DL	0.635		✓		

(*continued on next page*)

Table 2b (*continued*)

Site	Date	NO_3-N	NO_2-N	NH_4-N	Total N	no concern	possible contamination	cause for concern	above TV
		mg/l	mg/l	mg/l	mg/l	<0.2 mg/l N	0.2–1 mg/l N	>1 mg/l N	3 mg/l NO_3-N
MUPD	09/02/2022	0.554	<DL	0.002	0.557		✓		
MUPD	11/08/2022	0.494	<DL	0.048	0.542		✓		
MUPD	27/01/2023	0.608	<DL	0.017	0.625		✓		
MUPS	19/03/2021	3.314	0.244	0.011	3.57			✓	✓
MUPS	02/08/2021	0.394	0.057	0.892	1.34			✓	
MUPS	09/02/2022	1.480	0.081	0.003	1.56			✓	
MUPS	11/08/2022	3.835	0.108	0.242	4.19			✓	✓
MUPS	27/01/2023	2.580	0.081	0.015	2.68			✓	
Surface water									
Gauge 1	30/01/2018	0.711	<DL	0.179	0.890				
Gauge 1	02/02/2018	0.753	0.015	0.185	0.953				
Gauge 1	01/06/2018	0.432	0.040	0.021	0.493				
Gauge 1	11/10/2018	0.341	<DL	0.015	0.356				
Gauge 1	06/02/2019	0.962	<DL	0.047	1.01				
Gauge 1	27/06/2019	0.194	<DL	<DL	0.194				
Gauge 1	30/10/2019	0.532	0.009	0.101	0.642				
Gauge 1	05/02/2020	0.762	0.014	0.346	1.12				
Gauge 1	27/01/2023	1.162	0.011	0.190	1.36				
SW Nr 12	05/02/2020	<DL	<DL	<DL	<DL				
SW Nr 12	19/03/2021	<DL	<DL	0.012	0.012				
Eluted sand samples									
Sand1(PS)	Jun-18	0.96	0.023	n/s	–				
Sand2(PS)	Jun-18	0.17	0.027	n/s	–				
Sand3 (MU)	Jun-18	1.47	0.346	n/s	–				
Sand4(PS)	Oct-18	3.42	0.027	0.123	3.57				

buckthorn (Sand1(PS) (0.96 mg/l), Sand3 (MU) (1.47 mg/l) and Sand4 (PS) (3.42 mg/l) Table 2) when compared to the control site (Sand2(PS) (0.17 mg/l) Table 2). The Portstewart and Magilligan Umbra dunes are carbonate systems with dominantly calcium bicarbonate groundwaters with a near neutral pH (Table S2).

To investigate a causal link, the groundwater NO_3-N concentrations are plotted with the removal periods (arrows) (Fig. 2). For clarity, Portstewart piezometers have been grouped into those with NO_3-N below the TV concentration (PS2, PS4 and PS9, Table 2, Fig. 2b) and those with NO_3-N above the TV concentration (PS1, PS10 and PS12 Table 2, Fig. 2c and d). To illustrate the impact of removal of sea buckthorn local to piezometers (red arrow), PS1 (Fig. 2b) is plotted separately from PS10 and PS12 (Fig. 2c) due to their locations. Removal periods and locations are illustrated in Fig. 1 and the sites are discussed in section 4.

At Magilligan Umbra the most significant change to groundwater NO_3–N concentrations are seen at MUP4 which increased by 10.7 mg/l from 3.95 mg/l from just after the sea buckthorn removal to the next sampling event 10 months later (Table 2, Fig. 2a). However, the full extent of the peak may have been anywhere between February 2018 and February 2019 due to the sampling frequency. After the initial peak, nitrate concentrations started to reduce to below the TV approximately 2 years after removal (Table 2). Approximately 3.5 years after removal, total N concentration dropped to 'below concern' (Davy et al., 2010). There was a spike in total N concentrations at MUP4 to 'of concern' (Davy et al., 2010) in August 2022, which has since dropped to 'below concern'.

4. Discussion

4.1. Groundwater level response to the removal of sea buckthorn and Corsican pine

Infiltration through the unsaturated zone tends to occur in the autumn and winter when precipitation is greater than evapotranspiration and soil moisture reaches field capacity (Jones et al., 2006; Malcolm and Soulsby, 2001; Stuyfzand, 1993). The lag time for precipitation moving through the unsaturated zone to reach groundwater is likely to be different for each dune system, or area of the dune system due to soil moisture deficit, evapotranspiration, grainsize, depth of unsaturated zone etc. For instance at Merthyr Mawr Warren (South Wales, UK), studies on lag time showed seasonal variation with a complex series of lags and additional 1 day rapid response to daily rainfall (Jones et al., 2006). At a high dune site at Braunton Burrows UK it was estimated that infiltration rates in the unsaturated zone were in the order of 0.75–1 m/yr and recharge was due to piston flow (Allen et al., 2014).

The groundwater level at Portstewart and Magilligan Umbra at a given moment is the result of the preceding groundwater levels and effective rainfall. The height that the water table declines to during the spring – summer discharge period, influences the peak that it will reach because of the autumn – winter recharge period (Table 1).

During the period of monitoring, the groundwater hydrographs show that the groundwater levels at both sites are possibly higher than they would have been where it not for the vegetation removals (Wilson et al., 2022). It is also suggested that the shallow groundwater systems are receiving slightly more recharge due to a reduction in evapotranspiration caused by the removal of sea buckthorn and Corsican Pine trees (Figs. S1–S4, Wilson et al., 2022). However the monitoring period isn't long enough to provide a definitive causal link.

4.2. Unsaturated zone

The dissolved ions in infiltrating water depends on dry (gaseous and particulate) and wet (rainfall, sea spray, snow and occult) deposition at the dune site (Davy et al., 2006; Malcolm and Soulsby, 2001; Whiteman et al., 2010; Zunzunegui et al., 2024), the acidity of the infiltrating water, the minerals present in the dune system, plant derived inputs and the redox conditions. In a calcareous dune system such as Portstewart and Magilligan Umbra, the dominant ions are Ca and HCO_3. Infiltrating water increases leaching of dune soils due to their high permeability and low water storage capacity (Sevink, 1991).

Due to the build-up of sea buckthorn leaf litter and the production of nitrate by the sea buckthorn roots a 'store' of nitrate builds up in the unsaturated zone around the sea buckthorn (Binggeli et al., 1992;

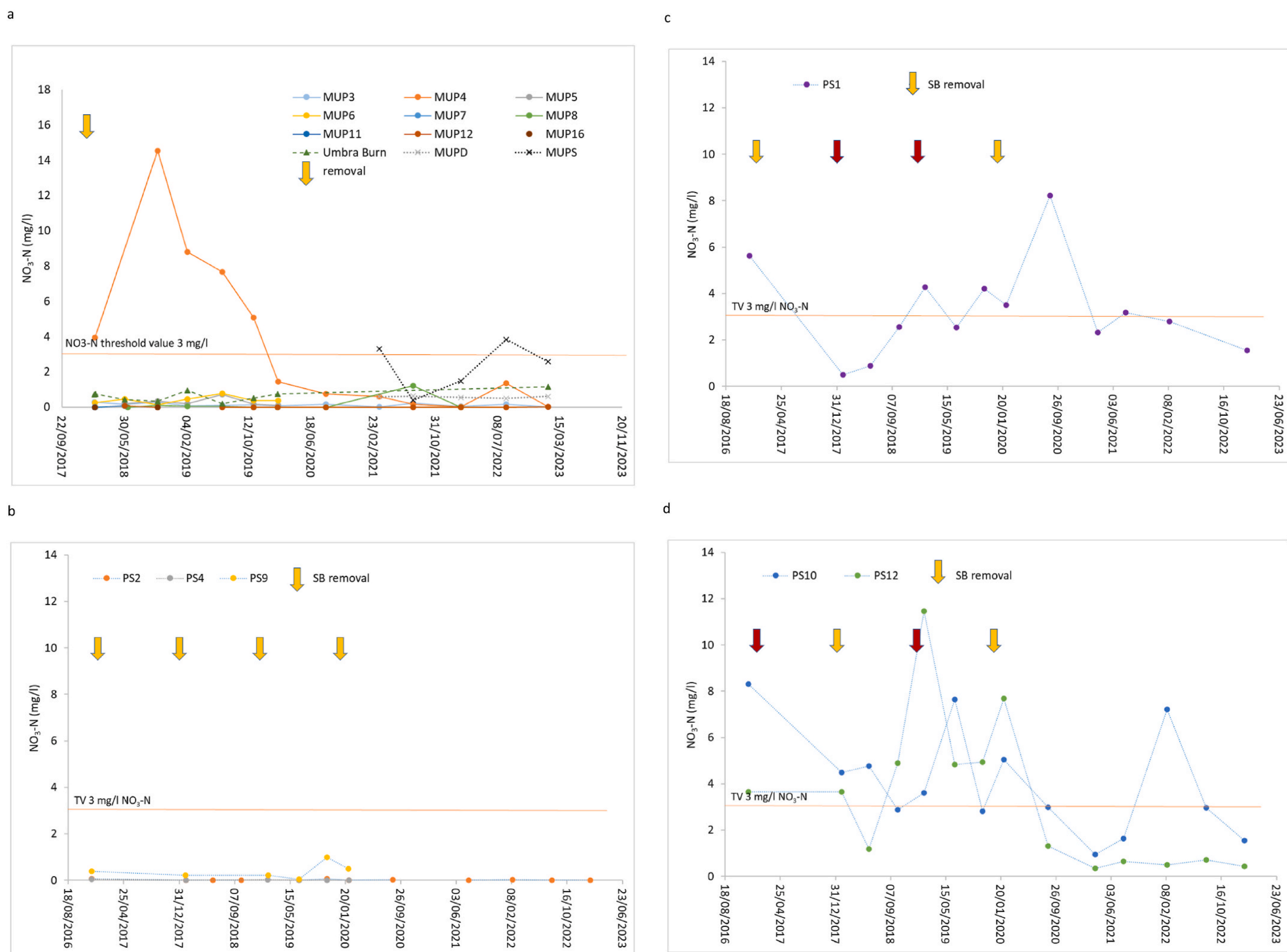

Fig. 2. Groundwater NO_3-N (mg/l) concentrations and sea buckthorn removal dates at Magilligan Umbra and Portstewart during the study period. a) Magilligan Umbra NO_3-N (mg/l). b) Portstewart NO_3-N (mg/l) at minimally impacted sites (PS2, PS4, PS9). c) sea buckthorn removal impacted site PS1 d) sea buckthorn removal impacted sites PS10 and PS12. Yellow arrows show site sea buckthorn removal occurrence and red arrows show local sea buckthorn removal periods. Contains GSNI data © Crown copyright and database rights 2024.

Stewart and Pearson, 1967). The eluted sand samples from the unsaturated zone at Portstewart and Magilligan Umbra (Table 2) corroborate previous studies; this clearly shows that the elevated concentration of NO_3-N in the unsaturated zone is free to infiltrate the aquifer.

Increased evapotranspiration due to the sea buckthorn (and Corsican pine trees) at the study sites may have led to reduced infiltration of ions into the aquifer prior to plant removal (McLenaghen et al., 1996). There is a seasonality to the available N in the soil zone. Stewart and Pearson (1967) observed soil NO_3-N and ammonium-N below sea buckthorn was greater in the winter compared to the summer and concentrations were inversely related to the amount of average monthly rainfall. Additionally, uptake of nitrogen from the soil is increased by non-nitrogen fixing plant growth in the summer (Davy et al., 2006). Once the sea buckthorn had been removed and the trees felled from Portstewart and Magilligan Umbra, evapotranspiration reduced, the plants no longer fixed nitrogen or used nitrate, and the ions were more available to infiltrate the unsaturated zone and into the aquifer. Additionally, soil disturbance due to the installation of piezometers and removal of sea buckthorn by the roots will have released ions into the unsaturated zone and eventually into the groundwater. Additionally, the ash from on-site sea buckthorn burning leads to point sources of nitrogen and other ions within the dune system (Denning et al., 2024). The short-lived flush of N and other ions from piezometer installation, is not seen at Magilligan Umbra due to the time elapsed between installation and the first groundwater sample; it is visible at Portstewart. However, at both sites the larger flush of N and other ions due to sea buckthorn removal is visible and is discussed below for each site. The removal of sea buckthorn removes a source of N within the system, and supplies within the unsaturated zone and groundwater will become depleted with time as shown at Magilligan Umbra and Portstewart.

4.3. Groundwater nitrogen changes due to removal of sea buckthorn and Corsican pine

Groundwater NO_3-N, and total N (NO_3-N, NO_2-N and NH_4-N) concentrations from Magilligan Umbra and Portstewart were compared with the guideline values of Davy et al. (2010) and Whiteman et al. (2017) to quantify the amount of nitrogen 'pollution' intercepting each piezometer (Table 2, Fig. 2) to monitor the effect of plant removal.

Available dissolved oxygen concentrations and the low concentrations of the redox sensitive ions Fe and As (Table S1) in shallow and deeper groundwater from most of the piezometers show a relatively well oxygenated dune groundwater, except at MUP12 and MUP8, where more reducing conditions were found. This points to the dominant form of groundwater nitrogen at Magilligan Umbra and Portstewart being NOx, however NH_4 dominates at MUP12 (Table 2).

4.3.1. Magilligan Umbra

Piezometers were installed over a year before the total removal of sea buckthorn and tree felling occurred at Magilligan Umbra in winter 2017/18 (Table 1) and groundwater sampling commenced within a month of removal (Table 2, Fig. 2a). The early installation of the piezometers allowed any impact of installation on groundwater chemistry to settle prior to sampling. The estimated groundwater flow direction (Wilson et al., 2022) indicates groundwater travelling through the sea buckthorn removal site only intersects piezometer MUP4 (Table 1) and that water from the Umbra Burn could theoretically flow into the dune system.

Groundwater NO_3-N increased significantly at MUP4 after the removal of sea buckthorn, decreasing to below the TV (Whiteman et al., 2017) approximately 2 years after removal and then, with slight fluctuation, to 'below concern' (Davy et al., 2010) approximately 4 years later.

Due to the groundwater flow direction (Fig. 1), the other shallow groundwater samples from Magilligan Umbra (MUP3, MUP5 to MUP8, MUP 11 and MUP 16 Fig. 2a) have been below the TV (Whiteman et al., 2017) during the project, however, the samples do, at times, show contamination as defined by Davy et al. (2010). Additionally, Rhymes et al. (2014) show an increase of nitrophilous species in dune slack wetlands at around 0.2 mg/l dissolved inorganic nitrogen, at the Davy et al. (2010) 'below concern'. The TV (Whiteman et al., 2017) is also high compared to Camargo and Alonso (2006) who suggest <0.5–1.0 mg/l TN to prevent aquatic ecosystems developing acidification and eutrophication and >2 mg/l NO_3-N for sensitive aquatic organism. MUP3 and MUP5 are very close to the removal area, but little elevation in total N occurred at these sites due to groundwater flow direction. Groundwater sampled from MUP12 is in the reduced form of NH_4, and shows no contamination (Davy et al., 2010).

The piezometers 'MUPS' and 'MUPD' installed and sampled from February 2020 gave access to the deeper groundwater in an area unlikely to be impacted by sea buckthorn. Total N concentrations from MUPD, show possible contamination (Table 2) as classified by Davy et al. (2010) while NO_3-N concentrations from MUPS were above the TV (Whiteman et al., 2017) twice out of the five times it has been quantified (Table 2). It has been previously shown that high nitrate concentrations can percolate to depth (Stuyfzand, 1993).

There is a causal link between the removal of sea buckthorn and increase in concentration of NO_3-N at MUP4 (Fig. 2), the only piezometer which intersects groundwater from the removal site. This is due to the leaching of N from remaining root nodules, ash, disturbance of the leaf litter and soil zone allowing more N to wash into the groundwater. Little to no impact has been seen at other piezometers, but there is an additional source of nitrogen contamination at the site. A pre-removal sampling baseline campaign would have helped to assess the full impact of the growing sea buckthorn and its removal on the groundwater total N concentrations. The additional nitrogen seen in the shallow and deeper groundwater could be from septic tanks or sewers servicing the dwellings on the dune system; it is not likely to be from the Umbra Burn in entirety as concentrations at MUPS far exceed those measured in the Umbra Burn. Nitrogen from leaking septic tanks or sewers is initially seen as ammonium but is oxidized to nitrite and then nitrate in oxic conditions as is seen at Magilligan Umbra (Gooddy et al., 2014; Wakida and Lerner, 2005).

There appears to be no influence on groundwater N concentration due to the felling of Corsican Pine on groundwater sampled from within the felled area (MUP11 or MUP 12). However, there is an increase in groundwater Cl, Na and SEC concentration at MUP12 (Table S2) and at MUP4 (Table S2) due to the disturbance of the dry deposition on the soil from the felling of trees and removal of sea buckthorn respectively.

4.3.2. Portstewart

The phased removal of the sea buckthorn complicates the data from Portstewart. For discussion, the piezometers have been grouped into those with NO_3-N below the TV concentration (PS2, PS4 and PS9, Table 2, Fig. 2b) and those with NO_3-N above the TV concentration (PS1, PS10 and PS12 Table 2, Fig. 2c and d). Dominant groundwater flow directions are estimated from groundwater level data (Wilson et al., 2022) and indicated on Fig. 1b.

4.3.2.1. Below TV. The shallow groundwater sampling sites PS2, PS4 and PS9 can be further classified. The groundwater below the golf course (PS2 and PS4 Fig. 1a and. 2b) has relatively low, stable total-N concentrations and the groundwater total N is classified as of 'no concern' (<0.2 mg/l N Davy et al., 2010). These are both in an area away from recent sea buckthorn removal sites. The golf course management during the time of the study had little to no negative impact on the groundwater nitrogen concentration.

Piezometer PS9 is in an area of sea buckthorn active growth, but removal has not occurred up groundwater flow from this site (Fig. 1b–Table 2). The variation in NO_3-N concentration within PS9 samples may reflect the natural variation of groundwater nitrate due to the growing sea buckthorn. Concentrations of total N show possible contamination as defined by Davy et al. (2010) in every sample except the one summer sample. Due to low groundwater level PS9 was only sampled once during the summer and eventually failed. We have too few summer measurements to conclude any seasonal effect at PS9, however these have been previously observed (Stewart and Pearson, 1967).

4.3.2.2. Above TV. PS1 was initially within an area of sea buckthorn and there have been two local removal events up groundwater flow of PS1 in winter 2017/2018 and winter 2018/2019 (Figs. 1b and 2c). The elevated total N concentration of December 2016 is likely to be due to the soil disturbance from the piezometers recent installation and subsequent infiltration of surface nitrate from dry deposition and sea buckthorn detritus. Peaks in groundwater NO_3-N concentration are seen approximately one year after removal of local sea buckthorn, although total-N concentrations have been decreasing since 2021, they are still a 'cause for concern' (Davy et al., 2010) 4 years after the last removal.

Removal of sea buckthorn surrounding both PS12 and PS10 occurred in winter 2016/2017 at the same time as the first sampling, the peak from these removals may have been lost as sampling was halted until January 2018. A second local removal occurred in winter 2018/2019 and a NO_3-N peak is observed within a few months at PS12, closest to the removal area, and a few months later at PS10, further from the removal area (Figs. 1b and 2c). Groundwater nitrate concentrations at PS12 appear to have settled since March 2021, however, another NO_3-N peak at PS10 was recorded in February 2022, possibly due to NO_3-N still travelling from a further removal point and intersecting PS10 (Fig. 1c). Due to the multistage removal close to these two piezometers, and hiatus in sampling, tracing the peaks is more complicated than at Magilligan Umbra. Additionally, the unsaturated zone depth at PS10 and PS12 is much deeper than at MUP4 (Table 1) due to topography which may lead to longer travel times through the unsaturated zone.

4.3.2.3. Overall. The spacing of the sampling events will have influenced where we see the peaks and troughs of nitrate concentration. Sampling became less frequent towards the end of the project.

At Magilligan Umbra and Portstewart the lag time between sea buckthorn removal and groundwater nitrate peak at an impacted piezometer was between a few months and about a year. The lag time will depend on the length of time for the bulk of the nitrate to travel through the unsaturated zone to the aquifer, the local groundwater flow rate and the distance between the removal point and the piezometer and sampling frequency. As the removal areas are often quite large the peak is an average arrival time, leading to more than one peak or an extended peak curve for one removal episode. Multiple removals in a similar area add further complication. The style of removal, groundwater infiltration rate through the unsaturated zone, the local occurrence of other nitrogen fixing plants, and mixing with older groundwater will affect the total N concentrations within the groundwater. Additionally, the growth of other dune flora, greater in the summer, may deplete the stored N in the soil and groundwater.

4.4. Likely sources of nitrate from dual nitrate isotopes

The isotopes of both the N (δ^{15}N-NO_3) and the O (δ^{18}O-NO_3) of nitrate or 'dual nitrate isotopes' have been used for decades as a signature for nitrate sources such as artificial fertilizers, the atmosphere, plants, animal manure and wastewater. However, global signatures are difficult to define due to local variation in climatic conditions and fractionation of the isotopes due to microbial denitrification in the aquifer (Böttcher et al., 1990), N_2-fixation and uptake of NO_3 by plants (Kohl and Shearer, 1980). Globally defined δ^{15}N-NO_3 and δ^{18}O-NO_3 signatures have large, overlapping ranges which do not help to define the source of nitrate within the studies samples.

However, more specific studies of isotopic data for plant fixed nitrogen and organic soil nitrogen do help define the data. Direct measurement of plant material by Shearer and Kohl (1986) gave the δ^{15}N of biologically fixed nitrogen as 0 ± 2‰. The δ^{15}N of organic soil nitrogen has been found to vary with mean annual temperature and mean annual precipitation (Amundson et al., 2003). However, modelled global soil data for Northern Ireland gives a δ^{15}N of organic soil N to a depth of 50 cm to be between 3.5 ‰ and 4.8 ‰ (Amundson et al., 2003). The current study derived δ^{15}N-NO_3 and δ^{18}O-NO_3 from nitrate within dune groundwater whereas Amundson et al. (2003) and Shearer and Kohl (1986) derived the δ^{15}N from total N.

Biologically fixed N originating from the sea buckthorn and soil N will both influence the isotopic signature of groundwater δ^{15}N-NO_3 and δ^{18}O-NO_3 at the studied sites (Fig. 3). A simplified model for the dune groundwater samples shows the sea buckthorn influenced sites (MUP3, PS1, PS10 and PS12) within the rough bounds of the biologically fixed nitrogen (Shearer and Kohl, 1986) with δ^{15}N-NO_3 varying between -2.8 ‰ and 1.3 ‰, whereas the more likely soil nitrogen influenced MUP6 and MUPD δ^{15}N-NO_3 are within the bounds of the modelled soil nitrogen for Northern Ireland (Amundson et al., 2003) at 4.2 ‰ and 4.9 ‰ (Fig. 3). The most direct comparison is seen between the eluted sand sample from beneath the sea buckthorn stand with a δ^{15}N-NO_3 of 1.4‰, comparable to that of biologically fixed N (δ^{15}N of 0 ± 2‰) (Fig. 3). Due to the method used it was difficult to fingerprint the groundwater and interstitial waters from areas unimpacted by sea buckthorn growth due to their low NO_3-N concentration. MUP3, PS1, PS10 and PS12 see a reducing influence of plant derived nitrogen over time due to the removal of the sea buckthorn and the dilution of any residual plant derived nitrogen within the unsaturated zone and groundwaters, this is highlighted by the δ^{15}N-NO_3 (and δ^{18}O-NO_3) becoming more positive

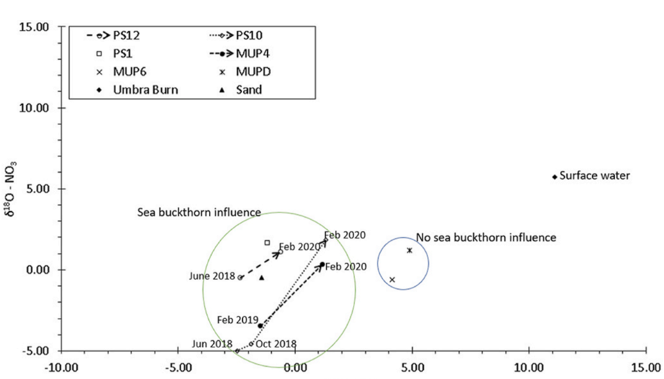

Fig. 3. Plot of δ^{15}N - NO_3 and δ^{18}O - NO_3 for groundwater, surface water and eluted sand samples from Magiligan Umbra and Portstewart. Contains GSNI data © Crown copyright and database rights 2024.

(Fig. 3). This evidences that microbial denitrification caused isotope fractionation at these sites as the isotopic signatures all became more positive in the same direction with time. This links well with the reduction in concentration of NO_3-N, and hence influence of sea buckthorn in groundwaters from these piezometers.

The isotopic signature of the Umbra Burn plots well away from the groundwater samples (Fig. 3). The nitrate sources within the burn are likely to be mixed; agricultural manure, fertilizers, and wastewater.

Further work to define the signature observed within the dunes would involve direct analysis of δ^{15}N-NO_3 and δ^{18}O-NO_3 from the sea buckthorn plant material, manure from grazing cattle, any N fertilizers applied direct to the golf course at Portstewart and the contents of the septic tank within the Magilligan Umbra site. An unsaturated zone profile below growing sea buckthorn would help to define where nitrogen is in the system and what the signature is. Additional sources of natural nitrogen will include nitrogen fixing blue-green algae found within flooded slacks, and other leguminous and non-leguminous nitrogen-fixing plants.

5. Conclusion

Groundwater from shallow piezometers at Magilligan Umbra and Portstewart were assessed for N contamination against the NO_3-N Threshold Value of Whiteman et al. (2017) and the indicator values for total nitrogen contamination of Davy et al. (2010). The Portstewart golf course had no growing or recently removed sea buckthorn and management practices were not seen to cause groundwater N contamination. Additionally, tree felling, without root removal, at Magilligan Umbra caused no noticeable increase in groundwater nitrogen concentration.

Growing sea buckthorn was shown to cause shallow groundwater N contamination when assessed against Davy et al. (2010), however, concentrations were low compared with areas that have seen active sea buckthorn removal. Eluted sand samples from the unsaturated zone of both dune sites confirm that sea buckthorn impacted areas have elevated N concentrations when compared to an unimpacted site.

Removal of sea buckthorn at both Magilligan Umbra and Portstewart was seen to significantly increase the groundwater nitrate concentration down groundwater flow of removal sites. The single sea buckthorn removal event at Magilligan Umbra in winter 2017/2018 caused groundwater nitrate to be above the TV for approximately 2 years and total N concentration became of 'no concern' (Davy et al., 2010) approximately 3.5 years after removal. Phased sea buckthorn removal at Portstewart complicated the response. However, the impact on groundwater N concentrations (specifically NO_3-N) was large, with an initial peak within one year of removal with the impact lasting several years.

This study is of importance to conservation management as it shows conclusive proof that the removal of sea buckthorn and burning at site will lead to a rapid increase in N contamination which will take several years to dissipate. The increased unsaturated and groundwater total N will lead to the growth of nutrient demanding species in the areas of sea buckthorn removal and further measures should be planned to manage this growth.

To decrease this impact, it is suggested that all sea buckthorn plant material, including roots and surface detritus, is removed from site during the removal phase to reduce the amount of available N to the ecosystem. Additionally, any subsequent nitrophile growth is to be removed from site.

CRediT authorship contribution statement

Debbie White: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Paul Wilson:** Writing – review & editing, Project administration, Methodology, Investigation, Funding acquisition. **Mark Cooper:** Writing – review & editing, Supervision, Funding acquisition. **Daren Gooddy:** Writing –

review & editing, Methodology, Conceptualization. **Kyle Hunter:** Writing – review & editing, Project administration, Methodology, Investigation, Funding acquisition. **Rebecca Ní Chonchubhair:** Writing – review & editing, Investigation.

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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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.indic.2025.100654.

Data availability

Data will be made available on request.

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