Public water supply is responsible for significant fluxes of inorganic nitrogen in the environment

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20   **Abstract**

21   Understanding anthropogenic disturbance of macronutrient cycles is essential for assessing risks

22   facing ecosystems. For the first time, we quantified inorganic nitrogen (N) fluxes associated with

23   abstraction, mains water leakage and transfers of treated water related to public water supply. In

24   England, the mass of nitrate-N removed from aquatic environments by abstraction (ABS-NO_3-N) was

25   estimated to be 24.2 kt N/yr. This is equal to six times estimates of organic N removal by abstraction,

26   15 times in-channel storage of organic N and 30 times floodplain storage of organic N. ABS-NO_3-N is

27   also between 3-39% of N removal by denitrification in the hydrosphere. Mains water leakage of

28   nitrate-N (MWL-NO_3-N) returns 3.62 kt N/yr to the environment, equating to approximately 15% of

29   ABS-NO_3-N . In urban areas, MWL-NO_3-N can represent up to 20% of total N inputs. MWL-NO_3-N is

30   predicted to increase by up to 66% by 2020 following implementation of treated water transfers.

31   ABS-NO_3-N and MWL-NO_3-N should be considered in future assessments of N fluxes, in order to

32   accurately quantify anthropogenic disturbances to N cycles. The methodology we developed is

33   transferable, using widely-available datasets and could be used to quantify N fluxes associated with

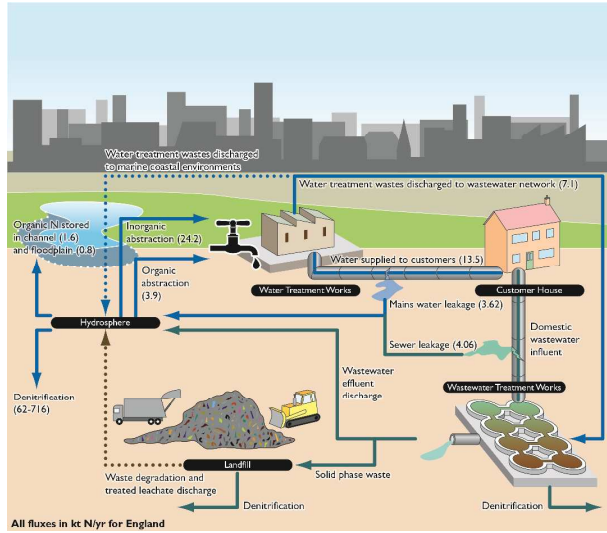34   public water supply across the world.

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43   **Abstract Art**

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60   **1   Introduction**

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62   Eutrophication associated with anthropogenic disturbance to nitrogen (N) and phosphorus (P) cycles

63   within aquatic ecosystems is a widespread environmental challenge that has been recognised for

64   over 50 years[1]. In response, substantial efforts have been made to reduce both point[2] and diffuse[3]

65   source nutrient inputs to the environment, for example through implementation of national and

66   international legislation (e.g the USA Clean Water Act[4], EU Water Framework[5], Nitrates[6] and Urban

67   Wastewater Treatment[7] Directives). Despite such efforts, there are multiple instances in which the

68   reductions in riverine concentrations and fluxes of N and P after the implementation of mitigation

69   activities have been lower than expected[8]. The release of nutrients, both from previously

70   unidentified sources and from legacy stores (e.g. groundwater, soils or the riparian zone[9]), is a

71   potentially important contributor to unexpected trajectories of catchment nutrient balances. In this

72   context, we sought to constrain the previously unquantified influence of public water supply on

73   inorganic N fluxes.

74   Recent research has suggested that the water treatment cycle (water abstraction, treatment,

75   distribution for public water supply and subsequent leakage) may have significant impacts on both

76   nutrient sources and nutrient retention, particularly in urban areas. For example, previous research

77   suggests that leakage of phosphate-dosed mains water (MWL-P) can be an important source of P in

78   urban environments, with MWL-P fluxes now reaching up to 24% of sewage treatment P loads in

79   some catchments[10-12].   Methods have also been developed to quantify N fluxes to groundwater

80   from mains water leakage at the city-scale[13-15], suggesting that approximately 36% of the total N

81   loads in urban areas could be attributed to this source.

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83   In the context of aquatic ecosystems, retention (also referred to as losses, sinks or removal) can be

84   conceptualised as transient (e.g. nutrient storage within floodplains or groundwater) or permanent

85   N removal (e.g. denitrification)[16]. Based on the difference between N fluxes from terrestrial to

86   aquatic ecosystems and N fluxes at the tidal limit of the fluvial system, Worrall, et al. [17] concluded

87   that substantial in-stream N retention occurs in Great Britain. Whilst detailed understanding of in-

88   stream retention mechanisms at the national-scale remains to be developed, it has been postulated

89   that these losses of N are primarily due to permanent N removal via denitrification[17]. However, the

90   processes associated with public water supply may also contribute significantly to N retention within

91   aquatic ecosystems. For example, Finlay, et al. [18] estimated the flux of organic N removed by water

92   abstraction, suggesting that this flux is greater than N retention associated with transient floodplain

93   storage.

94   However, important gaps remain in our understanding of how macronutrient fluxes are perturbed

95   by the processes associated with public water supply. Whilst Finlay, et al. [18] calculated organic N

96   removal, the mass of inorganic N removed during abstraction and the significance of this N retention

97   process relative to other forms of in-stream retention have not been quantified to date. Further,

98   previous methods developed for nutrient source apportionment either do not consider mains

99   leakage[19, 20], or use simplistic approaches[13-15] based on export coefficients and literature values

100   rather than observed leakage and concentration data. Finally, potential changes in inorganic N fluxes

101   due to mains water leakage associated with future treated drinking water transfers have not been

102   quantified. Water transfers are considered essential if future water demand is to be met, but the

103   water quality implications of water transfers remain poorly constrained[21]. If effective, integrated

104   approaches to the management of nutrient sources and fate are to be developed, it is essential that

105   future nutrient fluxes associated with water transfers are quantified and the locations where these

106   fluxes are significantly enhanced in the future are identified. Within this context, in the research

107   reported here we hypothesized that:

108   •   Abstraction of raw untreated water removes a significant, but spatially heterogeneous, mass

109   of nitrate (ABS-NO_3-N) from the aquatic environment (defined here as groundwater, rivers

110   and coastal marine environments);

111   •   A considerable proportion of ABS-NO_3-N is returned to the environment through leakage of

112   treated mains water containing nitrate (MWL-NO_3-N), particularly within urban areas;

113   •   Treated drinking water transfers will substantially alter the future magnitude and spatial

114   distribution of MWL-NO_3-N fluxes.

115   2   Materials and Methods

116   2.1   Study Area

117

118   The research reported here was developed at the national-scale for the country of England (Figure

119   1). Water is supplied by 21 water companies across England. Water company areas are divided into

120   water resource zones (WRZs) within which water supplies are largely self-contained[22]. These WRZs

121   are further divided into water supply zones (WSZs) which correspond to areas with uniform water

122   quality, supplying up to 100,000 people[23]. WSZs in England derived in this research (see supporting

123   information) and principal regions referred to in this research are shown in Figure 1.

124

125   2.2   Quantification of ABS-NO_3-N and MWL-NO_3-N

126

127   2.2.1   ABS-NO_3-N
128

129   We derived ABS-NO_3-N using estimates of the rates at which treated water enters the distribution

130   network from water treatment works (referred to herein as "distribution input") and raw water

131   quality data for each WSZ. Distribution input rates are not reported nationally at the WSZ level, so

132   these were derived as follows using estimates of treated water supplied to customers (referred to

133   herein as "water supplied"). The total distribution input, DI (m^3/day) into a WSZ was divided into

134   water supplied, S (m^3/day), and leakage, L (m^3/day):

$$DI = S + L \tag{1}$$

135   S for each WSZ was extracted from published data submitted by the drinking water regulator for

136   England to the European Commission[24]. For 12% of WSZs, values of S were not reported by the

137   drinking water regulator. For these WSZs, S was estimated using WRZ-level estimates of per capita

138   water consumption (PCC, L/h/d) published by Water UK [21] and the total population (P, unitless) for

139   each WSZ area, based on 1 km gridded population density mapping[25]:

$$S = \frac{PCC \cdot P}{1000} \tag{2}$$

140   Because WSZ-level leakage rates were not available, these were derived based on published WRZ-

141   level leakage rates[21]. Assuming that the percentage leakage rate in a WSZ is equal to the percentage

142   rate in the corresponding WRZ, L was derived as a fraction of the DI:

$$L = DI \cdot f_{WRZ} \tag{3}$$

143   where f_{WRZ} (unitless) is the fractional leakage rate of the WRZ. Combining equations (1) and (2), DI

144   was derived as:

$$DI = \frac{S}{1 - f_{WRZ}} \tag{4}$$

145

146   As no national scale datasets on WSZ raw water quality were available, mean raw water nitrate

147   concentrations for each WSZ were estimated using a heuristic approach based on data held in the

148   English environmental regulator's water quality monitoring database. Following previous studies of

149   national pollutant transport[11] and groundwater use maps[26], WSZs were classified as either

150   groundwater or surface water sources using national-scale hydrogeological mapping[27]. If a WSZ is

151   underlain by a moderate or highly productive aquifer, then the WSZ was considered to be a

152   groundwater WSZ. If underlain by a low productivity aquifer or rocks with essentially no

153   groundwater resource, then the WSZ was considered to be a surface water WSZ. For each WSZ, raw

154   water nitrate concentrations were estimated using the following rules: (1) only samples taken within

155   a WSZ; (2) only samples that correspond to the derived WSZ source water (i.e. groundwater or

156   surface water); (3) only samples taken in 2015 for direct comparability with drinking water quality

157   data for the same year (see section 2.2.2 and supporting information); and (4) only samples for

158   routine environmental monitoring, to avoid samples taken specifically for pollution investigations

159   unduly impacting the analyses. Where no water quality samples were present within a WSZ (4.5% of

160   WSZs in England by area) the mean raw water nitrate concentration of the nearest groundwater or

161   surface water sample point was used. Where WSZs are fed by existing water transfers, the receiving

162   WSZ was assigned the raw water nitrate concentration of the donor WSZ. After estimating DI and

163   raw water nitrate concentrations (C_R, mg N/L) for each WSZ, the mass of nitrate-N removed from the

164   aquatic environment through water abstraction, ABS-NO_3-N (kg N/day), was calculated as:

$$ABS\text{-}NO_3\text{-}N \ = \ \frac{C_R \cdot DI}{1000} \qquad (5)$$

165

166   **2.2.2   MWL-NO_3-N**
167

168   We calculated MWL-NO_3-N at the WSZ level using existing datasets for nitrate concentrations in

169   treated drinking water and the water supply rates and WRZ-level leakage rates detailed in section

170   2.2.1. Combining equations (3) and (4), L was calculated as:

$$L = \frac{S \cdot f_{WRZ}}{1 - f_{WRZ}} \qquad (6)$$

171   Nitrate concentration data were extracted from national-scale databases of WSZ drinking water

172   quality reports for 2015 (see supporting information). All water company laboratories are required

173   to be accredited by the UK Accrediation Service to the Drinking Water Testing Specification[28]. This

174   includes interlaboratory proficiency testing for all parameters including nitrate concentrations, and

175   thus any differences in nitrate concentrations between water companies associated with different

176   laboratory methods were assumed to be minimal. Using the mean treated drinking water nitrate

177   concentration for each WSZ for 2015, C_T (mg N/L), MWL-NO$_3$-N$_{WSZ}$ (kg N/day) was calculated as:

$$MWL\text{-}NO_3\text{-}N_{WSZ} = \frac{C_T \cdot L}{1000} \qquad (7)$$

178

179   **2.2.3   Changes in MWL-NO$_3$-N associated with future transfers of treated drinking water**
180

181   Transfers of treated drinking water at the WRZ-level that are planned to be implemented by 2020

182   were provided by the environmental regulator for England (Figure S1). These transfers are all located

183   in South East and Eastern England, where current water stress is greatest[21]. To assess the impact of

184   future transfers on the spatial distribution of MWL-NO$_3$-N, the WSZ-level MWL-NO$_3$-N$_{WSZ}$ estimates

185   derived in section 2.2.2 were aggregated to the WRZ level (MWL-NO$_3$-N$_{WRZ}$, kg N/day) to obtain a

186   baseline flux for 2015:

$$MWL\text{-}NO_3\text{-}N_{WRZ} = \sum MWL\text{-}NO_3\text{-}N_{WSZ} \qquad (8)$$

187   The impact of aggregation of WSZ MWL-NO$_3$-N fluxes to WRZ level, in addition to impacts of using

188   WRZ percentage leakage rates at the WSZ level and the impacts of estimating raw water nitrate

189   concentrations using national environmental regulator water quality databases, are considered in

190   section 4.3.

191

192   For each water transfer, the future leakage rate for the transferred water in the receiving WRZ was

193   assumed to equal the existing leakage rate in the receiving zone. This is a reasonable assumption

194   because all water companies in England have current leakage rates at or below the sustainable

195   economic level of leakage[29] and leakage rates are not forecast to change substantially over the next

196   25 years[21, 30]. The volumetric leakage rate for a transfer, L_T (m^3/day), can therefore be estimated as:

$$L_T = DI_T \cdot f_R \tag{9}$$

197   where f_R is the leakage fraction (unitless) for the receiving WRZ and DI_T (m^3/day) is the additional

198   distribution input associated with the transfer. The nitrate concentration in the transferred water in

199   the future was assumed to equal to the current drinking water nitrate concentrations in the donor

200   WRZ. Nitrate concentrations in drinking water in England are consistently below the European

201   drinking water standard, with 99.99% of test samples compliant[31]. Consequently, there is unlikely to

202   be any additional treatment for nitrate removal associated with future treated water transfers. The

203   flux of N from mains water leakage associated with an individual planned transfer, MWL-NO_3-N_T (kg

204   N/day), was estimated as:

$$MWL\text{-}NO_3\text{-}N_T = L_T \cdot C_{T-D} \tag{10}$$

205   where C_{T-D} is the mean treated drinking water nitrate concentration in the donor WRZ (mg N/L).

206   Some WRZs are expected to receive a number of different water transfers in the future. In these

207   cases, the individual transfers were combined to derive the total additional flux of N from mains

208   leakage resulting from all transfers, MWL-NO_3-N_{WRZ-T} (kg N/day):

$$MWL\text{-}NO_3\text{-}N_{WRZ-T} = \sum MWL - N_T \tag{11}$$

209   Using the baseline WRZ-level estimates of MWL-NO_3-N_{WRZ} for 2015, the percentage change in MWL-

210   NO_3-N_{WRZ} expected after the implementation of the planned transfers by 2020, ΔMWL-NO_3-N_{WRZ}

211   (unitless) was calculated as:

$$\Delta MWL\text{-}NO_3\text{-}N_{WRZ} = \frac{MWL\text{-}NO_3\text{-}N_{WRZ-T} + MWL\text{-}NO_3\text{-}N_{WRZ}}{MWL\text{-}NO_3\text{-}N_{WRZ}} \cdot 100 \tag{12}$$

10

212

2.3   Comparison between ABS-NO$_3$-N, MWL-NO$_3$-N and estimates of other N

sources and N retention in the aquatic environment

215

216   Our estimates of ABS-NO$_3$-N were compared with previous, national-scale estimates of the retention

217   of organic N via water treatment for public supply, floodplain storage and in-channel storage[18]. We

218   also compared ABS-NO$_3$-N with estimates of N removal via denitrification in the entire English

219   hydrosphere (groundwater, surface water and the coastal marine environments)[32] and total in-

220   stream losses (assumed to be dominated by denitrification)[17]. Organic N retention by abstraction

221   was reported as a per-capita flux which was transformed to a total flux for England using the current

222   population of England[33] . All other fluxes were reported either as an absolute flux or flux per unit

223   area. Where necessary, fluxes at the scale of England were calculated using the percentage of the

224   UK land area which England comprises (54%).

225

226   To quantify the significance of MWL-NO$_3$-N, this flux was compared with other datasets aggregated

227   to both the national and the WRZ level. To compare with previous estimates of urban N fluxes, we

228   used estimates of N fluxes to groundwater at 1 km grid scale from water mains and the sewer

229   network derived by the UK Environment Agency [34] following the export coefficient approach of

230   Lerner [14]. We also used previous catchment-scale estimates of both urban diffuse (roads, residential

231   zones, open urban spaces, industrial and commercial areas) N fluxes to rivers and from all N sources

232   provided under the SEPARATE framework[20]. We calculated ratios of both current and future (post-

233   transfers) MWL-NO$_3$-N made in our research to these estimates of N inputs from other sources.

234   ## 3   Results

235

236   ### 3.1   ABS-NO$_3$-N

237

238   Figure 2 reports the spatial distribution of ABS-NO$_3$-N across England. Blank areas denote locations

239   in which no public water supplies are present (typically in sparsely populated upland areas in the

240   north of England) or where data were unavailable (a small number of WSZs in southern England).

241   Substantial spatial variation in the distribution of ABS-NO$_3$-N is revealed, with ABS-NO$_3$-N broadly

242   greater in the Midlands and the South East than in the far North and Southwest of England. There

243   are also additional hotspots of high ABS-NO$_3$-N in Yorkshire and the Humber, the West and East

244   Midlands and near to London. The broad spatial trends and the hotspots are primarily related to

245   variations in ABS-NO$_3$-N associated with high nitrate concentrations in some raw groundwaters and

246   surface waters.

247

248   Table 1 reports national-scale estimates of ABS-NO$_3$-N for England in comparison to previous studies

249   estimating N retention in aquatic environments in England. For 2015, we estimated total ABS-NO$_3$-N

250   for England to be 24.2 kt N. Finlay, et al. [18] suggest that the total mass of organic N removed during

251   water abstraction for public supply in the UK is 0.07 kg N/h/yr, equating to a total flux in England of

252   3.9 kt N/yr. ABS-NO$_3$-N therefore removes approximately six times more N from the environment as

253   nitrate than is associated with abstraction of organic N. ABS-NO$_3$-N is also 30 and 15 times greater

254   than N storage in floodplains and in channels as organic N respectively. The range of estimates for

255   the magnitude of denitrification within aquatic environments in England is substantial, from 62 kt

256   N/yr for the complete hydrosphere (surface water, groundwater and marine coastal environments)[32]

257   to 716 kt N/yr within the stream network alone[17]. Based on this range of available estimates, ABS-

258   NO$_3$-N is equivalent to between 3 – 39% of current estimates of denitrification in aquatic

259   environments.

260   **3.2   MWL-NO$_3$-N**

261

262   The distribution of MWL-NO$_3$-N across WSZs in England is reported in Figure 3. Substantial spatial

263   variation is also revealed in the MWL-NO$_3$-N fluxes, reflecting both the spatial distribution of leakage

264   rates and drinking water nitrate concentrations. Significant N fluxes from mains leakage are present

265   in urban areas with high leakage rates such as London, the West Midlands and the Humber.

266   Relatively high MWL-NO$_3$-N fluxes are also observed in Eastern England and along parts of the south

267   coast, where particularly high nitrate concentrations have been observed in drinking water.

268

269   Table 2 reports the total MWL-NO$_3$-N flux for England alongside previous national-scale N flux

270   estimates. The estimate of national-scale MWL-NO$_3$-N in our research (3.62 kt N/yr) is significantly

271   below previous estimates of this flux made by the Environment Agency [34] and relatively similar to

272   estimates of fluxes from sewer leakage (4.07 kt N/yr). Based on previous N source apportionment

273   studies (SEPARATE[20]), the return of MWL-NO$_3$-N to the environment is small (c. 1%) at the national-

274   scale relative to all other N sources, but much more significant (c. 160%) relative to urban diffuse N

275   sources.

276

277   Figure 4 reports our estimates of MWL-NO$_3$-N as a percentage of the total N flux from all sources

278   derived from Zhang, et al. [20], aggregated to the WRZ level. MWL-NO$_3$-N is generally small relative to

279   total N fluxes, at 2 – 5% of the total flux in the majority of WRZs in Southeast England and the

280   Midlands. MWL-NO$_3$-N is <1% in large WRZs in Northern, Southwest and Eastern England, where

281   agricultural land is extensive and urban areas are small relative to the total land area. However, in

282   London and the surrounding area where urban land area is more extensive, MWL-NO_3-N grows in

283   significance. For example, MWL-NO_3-N fluxes are estimated to be c. 15%, 16% and 20% of total N

284   sources in WRZs in London, the south coast and Kent (east of London) respectively.

285   ## 3.3   Changes in MWL-NO_3-N associated with future treated water transfers

286

287   Figure 5 reports the percentage change in the MWL-NO_3-N flux in receiving WRZs after

288   implementation of planned treated water transfers by 2020. In some WRZs on the south coast of

289   England, MWL-NO_3-N fluxes are predicted to increase by up to 66% compared to 2015 levels,

290   although implementation of water transfers is generally predicted to increase MWL-NO_3-N fluxes by

291   a relatively small amount (5 – 15%) compared to the 2015 baseline. MWL-NO_3-N remains small

292   relative to other N sources in the majority of WRZs where transfers are implemented. However, in

293   WRZs to the west of London, MWL-NO_3-N is expected to rise after the implementation of planned

294   water transfers to the equivalent to up to 20% of all N sources (Figure S2).

295   # 4   Discussion

296   ## 4.1   ABS-NO_3-N: A significant sink for N within the environment?
297

298   Nitrogen retention within the aquatic environment contributes to the differences between the N

299   flux from the terrestrial biosphere and the fluvial flux of N to the oceans[35]. Assuming net growth and

300   decay of riverine biota at the national-scale is negligible[17], denitrification has previously been

301   considered the primary mechanism for N removal in aquatic ecosystems[36, 37]. Only recently has

302   research begun to quantify direct N removal from the environment through anthropogenic

303   processes such as water abstraction[18].   In the context of N retention, a significant unique

304   contribution of our research is the quantification of nitrate removed from aquatic environments by

305   water abstraction, which is a significantly greater N flux than the estimate of organic nitrogen

306 removal by abstraction, storage within floodplain and in-channel environments by Finlay, et al. [18].

307 The wide range of estimates for the magnitude of aquatic denitrification means that quantifying the

308 relative importance of ABS-NO_3-N is challenging. Further research is needed to better constrain

309 these highly variable estimates to more accurately evaluate the significance of ABS-NO_3-N.

310 Nevertheless, given that the upper limit for ABS-NO_3-N represents c. 40% of denitrification in the

311 hydrosphere of England, including ABS-NO_3-N in future catchment N budgets appears to be

312 important.

313

314 Whilst ABS-NO_3-N removes significantly more N than is associated with abstraction of organic N, and

315 may also be significant relative to the N flux associated with denitrification, ABS-NO_3-N may only

316 represent a transient retention process. The ABS-NO_3-N flux can be divided into: (1) N removed by

317 water treatment processes; (2) N lost through mains water leakage; and (3) N supplied within

318 treated water that reaches households. Mains water leakage will return N directly into the

319 environment, although it is likely to be delayed before finally reaching receiving waters. Using

320 drinking water nitrate concentrations and the WSZ supply rates estimated in this research, we

321 estimate that 13.5 kt N/yr enters treated public water supply. Based on the difference between ABS-

322 NO_3-N and the sum of MWL-NO_3-N and N in treated public water supply, we estimate that 7.1 kt

323 N/yr is removed by the treatment of raw water before distribution. Much of the N that enters

324 treated water will ultimately move into the wastewater network[38]. Waters that are highly enriched

325 in nitrate produced by nitrate removal from raw water through ion exchange during drinking water

326 treatment will also enter the wastewater network, although in coastal areas direct discharge to the

327 marine environment may occur[39]. Following wastewater treatment, N will be partitioned between

328 solid phase waste sent to landfill or returned to agricultural land and dissolved or particulate N

329 discharged directly to receiving waters. Whilst these processes are likely to have varying timescales

330 for return of N into the environment, critically they are all likely to be substantially longer than the

331   mean residence time for water within UK rivers (26.7 hrs[18]). Therefore, whilst ultimately a transient

332   retention processes, ABS-NO_3-N will significantly alter the spatial and temporal distribution of N

333   inputs into aquatic ecosystems.

4.2   MWL-NO_3-N: A significant N source in urban areas

335

336   At the national-scale, our research suggests that MWL-NO_3-N is equal to approximately 15% of ABS-

337   NO_3-N. This is likely to be reasonable because leakage rates in England have been reported to be up

338   to 20% of water entering the distribution network[10] and treated waters show substantial variation in

339   nitrate concentrations. MWL-NO_3-N is small compared to all other N sources in large WRZs, where

340   agriculture is the most significant N source. However, in urban areas MWL-NO_3-N may account for

341   up to 20% of all N loads. These findings are broadly consistent with initial city-scale studies reported

342   previously for Nottingham, UK[15]. Previous work that adopts relatively simple estimates of MWL-NO_3-

343   N using export coefficient approaches[34] substantially overestimates MWL-NO_3-N compared to our

344   approach which uses observed leakage and concentration data. The flux of N associated with MWL

345   should be considered in more detail in urban N source apportionment studies. The methodology we

346   report here is transferable and could be applied where the necessary data are available, delivering a

347   significant increase in accuracy and spatial resolution of estimates of MWL-NO_3-N compared to

348   alternative approaches.

349

350   Previous research has suggested that incorporation of the environmental cost of P fluxes from mains

351   water leakage within methodologies to estimate the sustainable economic level of leakage (SELL)

352   could result in more stringent leakage targets, and consequently lower P fluxes to the

353   environment[12]. Extending the SELL approach to consider the environmental impact of MWL-NO_3-N

354   would also be of environmental benefit. However, whilst MWL-NO_3-N represents a substantial N

355   flux to the environment, concentrations in mains leakage are lower than in sewer leakage[13].

356   Consequently, mains leakage to groundwater may dilute high nitrate sewer leakage. Integrating N

357   sources into SELL would require an evaluation of the tradeoff between the negative environmental

358   impact of MWL-NO_3-N as an N source and any environmental benefit associated with dilution of

359   sewer N leakage. Additional nitrate removal from raw waters to reduce MWL-NO_3-N fluxes whilst

360   continuing to dilute sewer N leakage is unlikely to be a viable solution, given that concentrations of

361   nitrate in drinking water within England are already below the European drinking water standard[31].

362

363   It should be noted that MWL-NO_3-N, rather than representing a new input of reactive N to the

364   terrestrial environment (as would be associated with the application of inorganic N fertilisers or N

365   fixation for example), instead represents a return of N to the environment after water abstraction.

366   Return of N via MWL therefore represents a potential alteration to the distribution and residence

367   time of N in different environmental compartments. In this context, it should also be noted that the

368   ultimate fate of MWL-NO_3-N currently remains uncertain. The MWL-NO_3-N flux may be mediated by

369   the soil microbial community and by plants following leakage. MWL-NO_3-N may also be subject to

370   denitrification, although this is unlikely near to the site of a leak as treated water has been shown to

371   be low in organic carbon[23] and is unlikely to be anaerobic due to oxidation processes during water

372   treatment (e.g. ozonation producing dioxygen[40]) and extensive contact with the atmosphere[41]. It is

373   likely that the fate of MWL-NO_3-N can be broadly divided between fluxes to groundwater, surface

374   water and the sewer network. Based on the national-scale hydrogeological mapping described in

375   section 2.2.1, the MWL-NO_3-N flux on moderate and highly productive aquifers is estimated to be

376   1.67 kt N/yr. Given the long residence times in the unsaturated and saturated zones[42, 43], it is likely

377   that legacy MWL-NO_3-N from previous decades has accumulated within both groundwater and the

378   vadose zone, as has been observed for nutrient loads from agricultural land[44-46].   Moreover,

379   historical leakage rates have been significantly higher than at present, with rates falling by a third

380 between 1994 and 2015[47]. Consequently, the rate of MWL-NO$_3$-N accumulation within the vadose

381 zone and groundwater is likely to have been greater in the past compared to the present day.

382

383 Our research predicts relatively small changes in the spatial distribution of MWL-NO$_3$-N fluxes

384 associated with treated drinking water transfers. These transfers are fully costed, planned and will

385 be implemented by water utilities by 2020 in England. Larger-scale transfers which may result in

386 larger differences in water quality (and changes in MWL-NO$_3$-N fluxes) are currently being

387 evaluated[21], although these transfers are yet to be formally included in the water resources plans.

388 However, it should be noted that for both planned and speculative transfers of treated water,

389 implementation of additional treatment for nitrate removal is unlikely because concentrations are

390 already below the European drinking water limit. With mitigation measures to control other N

391 pollution sources being implemented[48], and limited changes planned for mains water leakage

392 rates[30], it is likely that the relative significance of MWL-NO$_3$-N will increase in the future, as has been

393 reported for MWL-P in the Thames catchment[30].

394

395 **4.3   Local and global research priorities for ABS-NO$_3$-N and MWL-NO$_3$-N**
396

397 The unique contribution of this study is the first national-scale estimates of N fluxes from abstraction

398 and mains water leakage using observed nitrate concentration and leakage data, both before and

399 after the implementation of future water transfers. There are a number of outstanding research

400 priorities within this field which remain to be addressed. To date the only published national

401 estimates of aquatic N retention by abstraction are for organic N compounds[18], and comparing ABS-

402 NO$_3$-N with other temporary retention processes that influence inorganic N would be helpful. Our

403 research has quantified the flux of nitrate associated with water treatment processes as the

404   difference between ABS-NO$_3$-N and the sum of MWL-NO$_3$-N and N in treated water supplied. Direct

405   quantification of N removal during water treatment at the national-scale using observed

406   concentration and flow data for process losses could be used to further validate the approach

407   reported here. Water abstraction for public supply is also likely to be associated with significant

408   fluxes of other inorganic N species, for example meaning that quantifying the mass of N removed via

409   abstraction of ammonium may also be important.   Further research should also evaluate the

410   ultimate fate of MWL-NO$_3$-N and the timescales for re-release of N to the environment from

411   transient stores associated with the water treatment cycle.

412

413   The research reported here at the national-scale highlights the particular importance of MWL-NO$_3$-N

414   in urban areas. However, due to the dearth of data at the WSZ level, there are a number of

415   uncertainties in this study which should be considered when evaluating future research priorities. It

416   should be noted that WSZ level leakage rates were estimated by applying percentage leakage rates

417   from the corresponding WRZ. Whilst treated drinking water nitrate concentrations are reported at

418   the WSZ level, there is likely to be some uncertainty in estimates of raw water nitrate concentrations

419   as these have been made based on environmental regulator water quality databases and a heuristic

420   assessment of water sources based on hydrogeological mapping and existing water transfers.

421   Treated drinking water transfers are reported at the WRZ level and thus the impact of transfers on

422   MWL-NO$_3$-N fluxes has been reported at the WRZ level in this research. As a consequence of these

423   factors, it is plausible that there may be more detailed local variability in MWL-NO$_3$-N, ABS-NO$_3$-N

424   and the impact of treated water transfers in urban areas than reported in this research. Additional

425   local-scale work should focus on these areas, drawing on datasets such as detailed raw water quality

426   data, District Metering Area leakage data and information on water transfers.

427

428   Further research to quantify both ABS-NO_3-N and MWL-NO_3-N fluxes globally is also likely to be of

429   importance. For example, water abstraction for all uses at the global-scale has been estimated at c.

430   4000 km^3/yr in 2010[49]. Using a conservative assumption that nitrate concentrations in raw

431   abstracted water are half of the World Health Organisation guideline value (i.e. 5.65 mg N/L), global

432   ABS-NO_3-N would remove 22.6 Tg N/yr from the aquatic environment. This is equivalent to between

433   5 and 39% of denitrification in soils, groundwater and riparian zones globally[50]. Global leakage rates

434   have been estimated at 32 billion m^3/yr[51]. Assuming the same nitrate concentration in leakage as in

435   treated drinking water, leakage of N would contribute 0.525 Tg N/yr into the environment. This

436   equates to approximately 1% of the global leaching and riverine N flux[52]. Whilst small in absolute

437   terms, this ratio at the global-scale is similar to that reported above for England. Given the

438   significance of MWL-NO_3-N in urban areas in England we report above, it is plausible that MWL-NO_3-

439   N may be a significant N source in urban areas across the world. Further, both ABS-NO_3-N and MWL-

440   NO_3-N may be more significant N fluxes in developing countries where nitrate concentrations and

441   leakage rates[51] are likely to be higher than those reported here for England[53]. Therefore, accurately

442   quantifying N fluxes associated with public water supply represents an important challenge to be

443   addressed across the globe.

444

445

446

447   **5 Acknowledgements**

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452

6   Supporting Information

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454

455   *Methodology for Water Supply Zone mapping and extraction of treated drinking water nitrate*
456   *concentration data*

457   *Figure S1 Location of planned treated drinking water transfers by 2020 and receiving water resource*
458   *zones (WRZs) in England*

459   *Figure S2 MWL-NO$_3$-N as a percentage of all N sources (as derived from) in receiving WRZs following*
460   *implementation of treated drinking water transfers by 2020*

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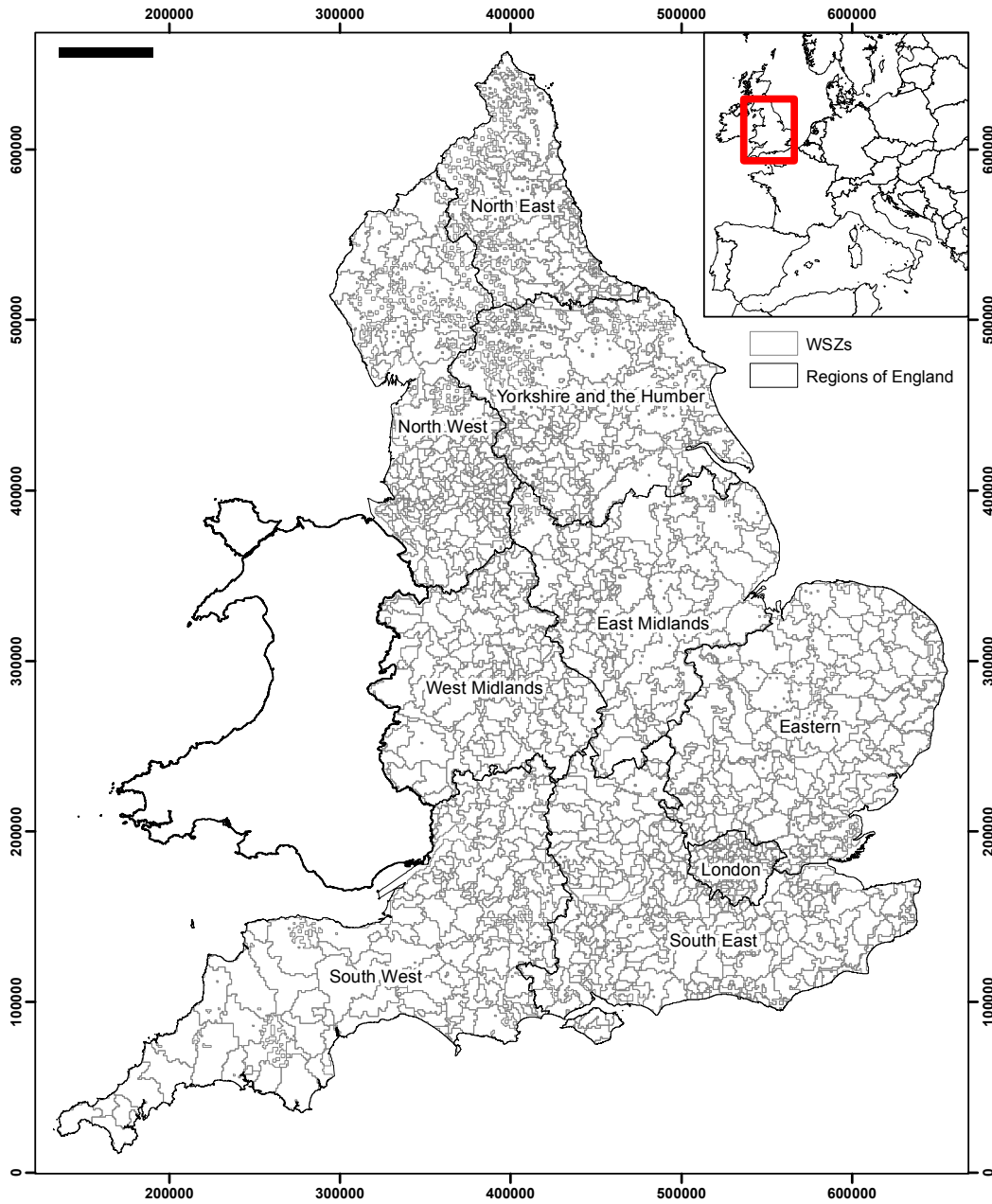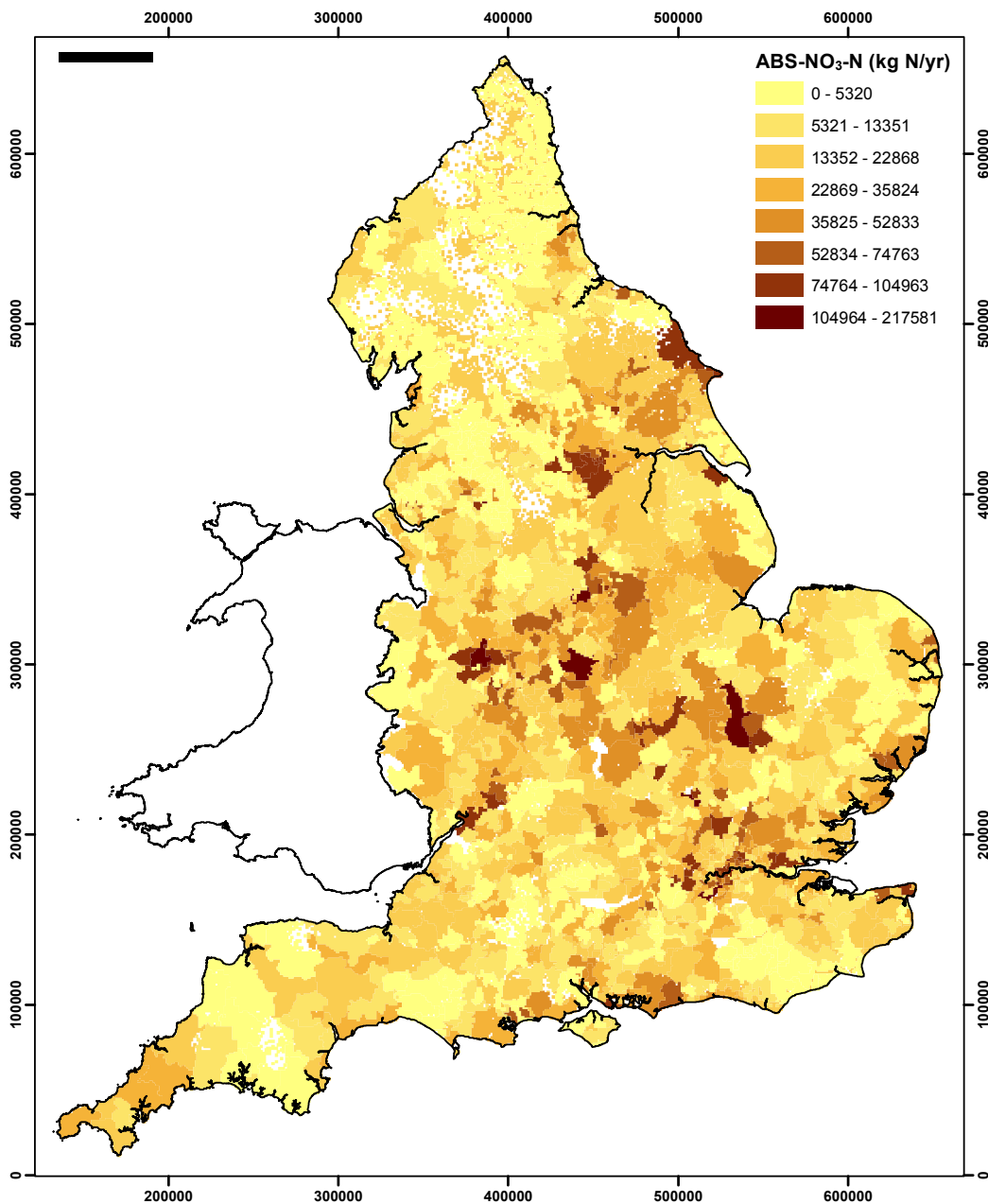635
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Figures

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648   *Figure 1 Water Supply Zones (WSZs) and principal regions in England*
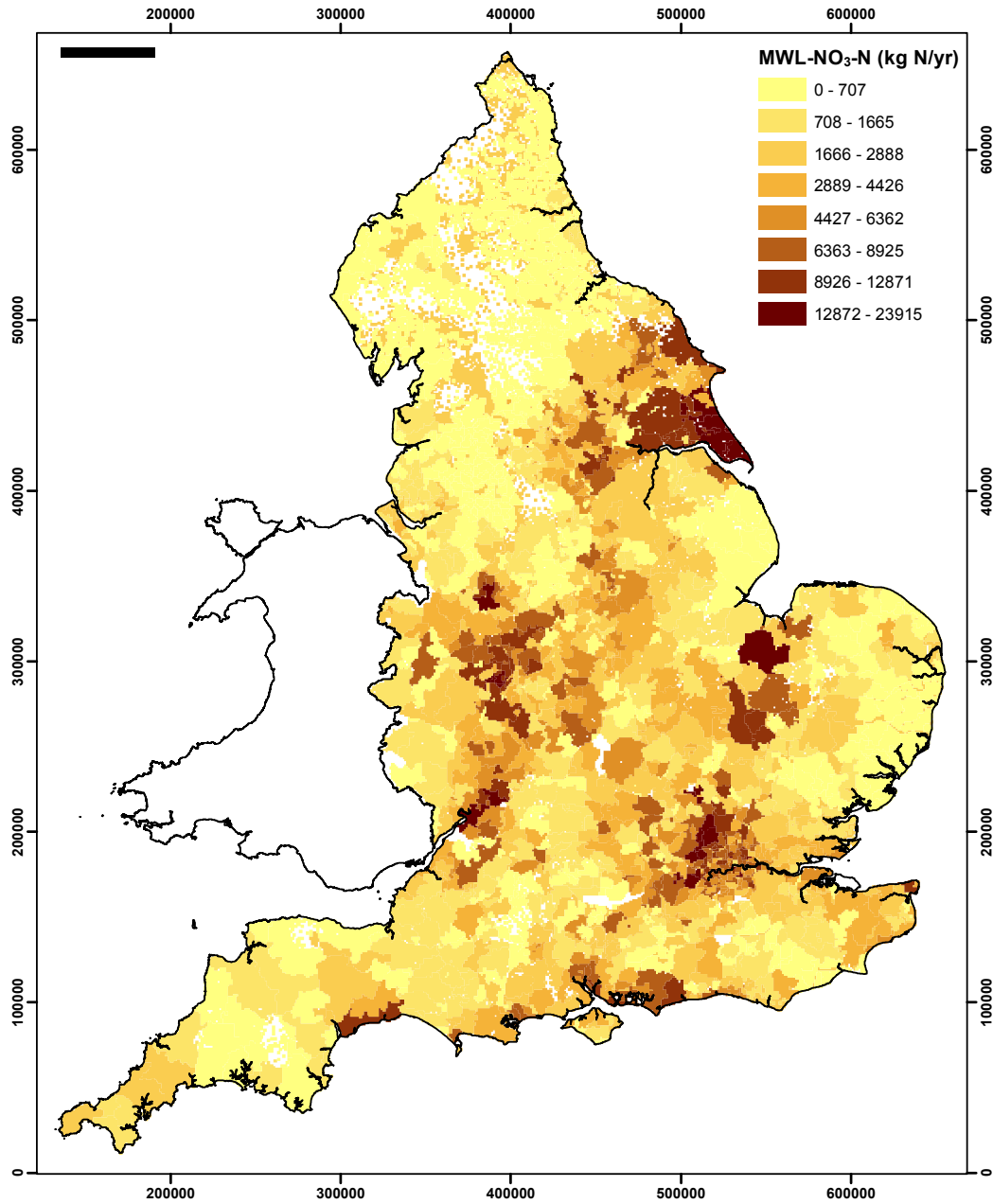
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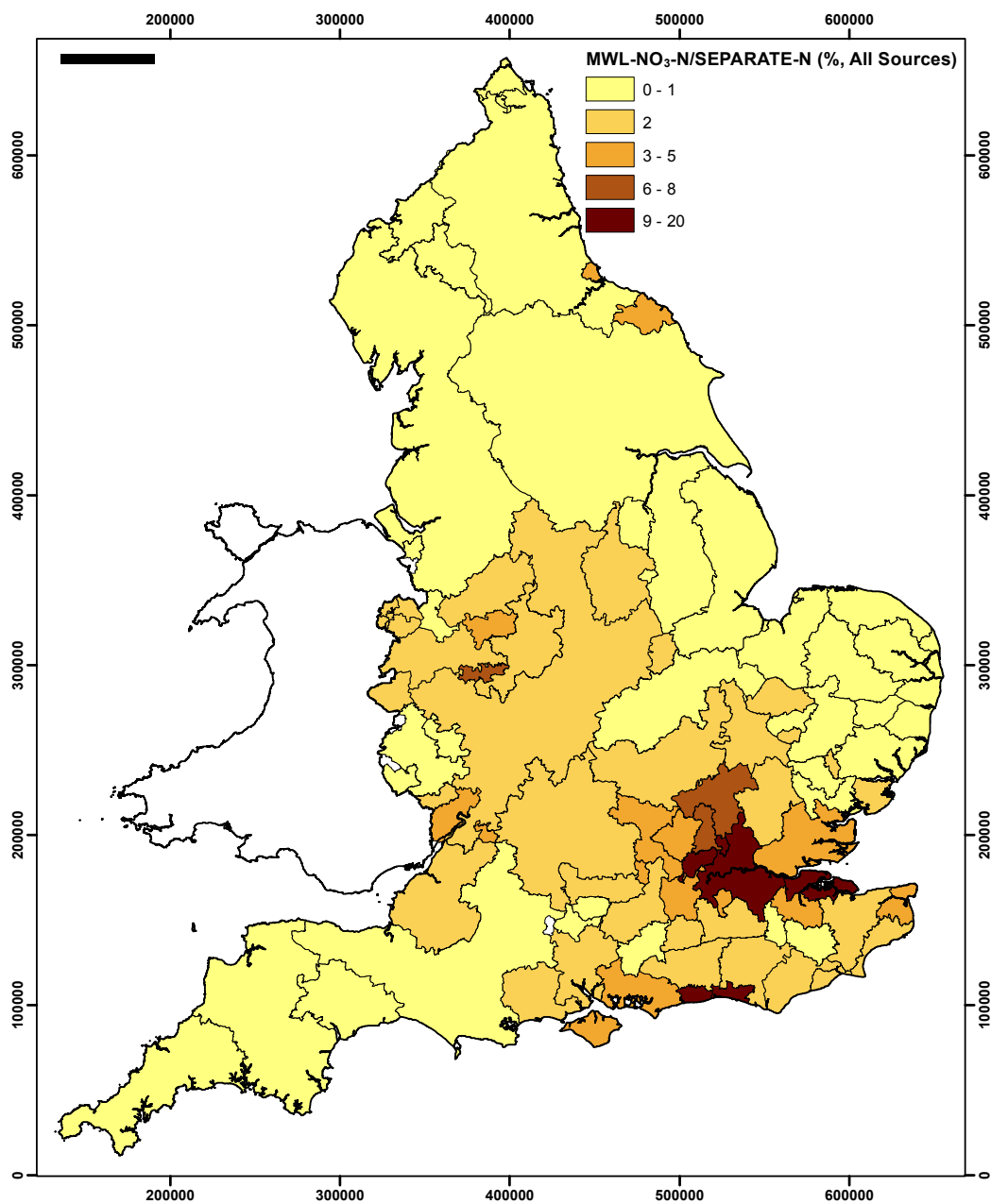651   *Figure 2 Distribution of ABS-NO$_3$-N in England for 2015*

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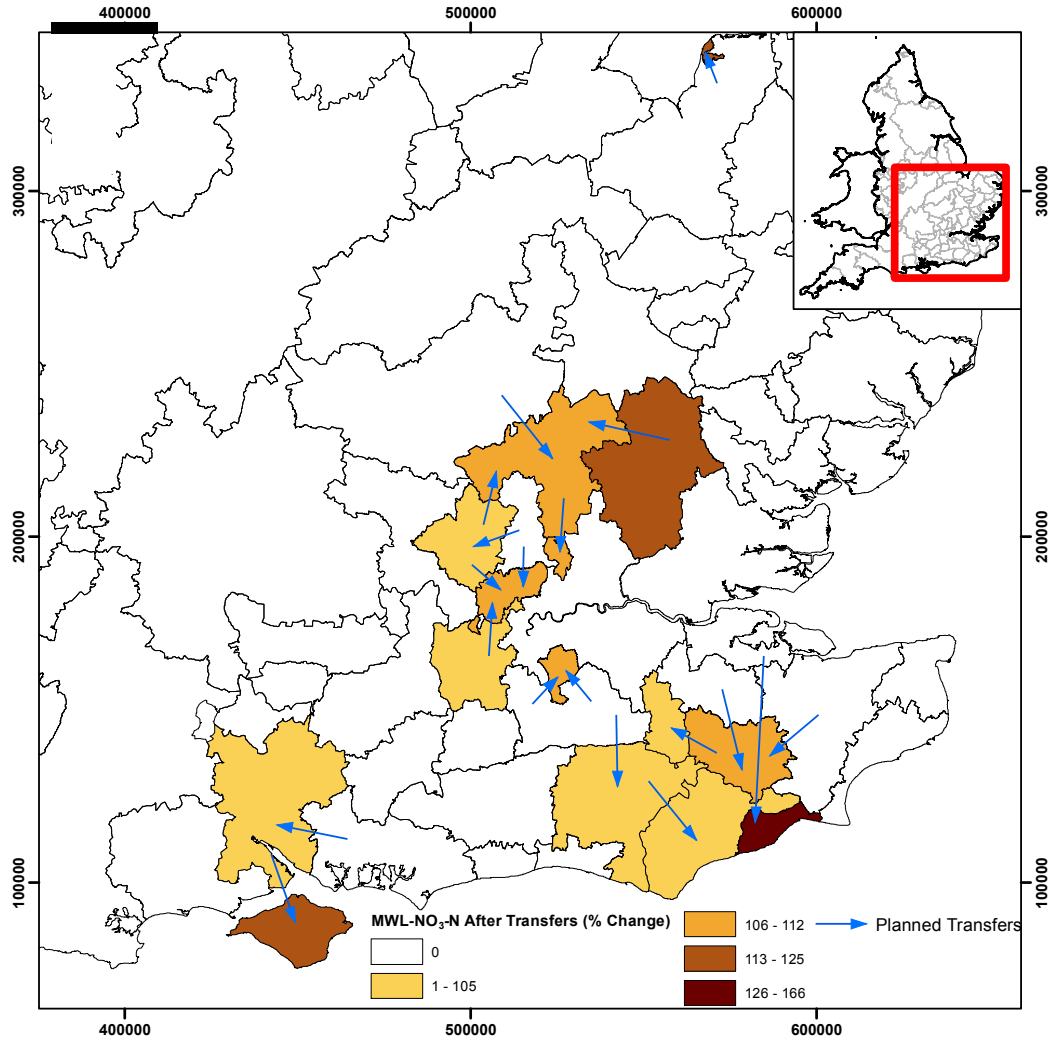655   *Figure 3 MWL-NO$_3$-N fluxes for WSZs in England for 2015*

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657   *Figure 4 Percentage of MWL-NO₃-N to all N sources (as derived from SEPARATE[20]) at the WRZ scale in England for 2015*

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662   *Figure 5 Percentage change in MWL-NO$_3$-N flux compared to 2015 baseline in receiving WRZs following implementation of*
663   *treated drinking water transfers by 2020*

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671 **8 Tables**

672

673 *Table 1 Total flux of nitrate removed from the aquatic environment by abstraction (ABS-NO$_3$-N) in England for 2015 in*
674 *comparison to previous estimates of aquatic N retention (organic N retention and storage) and removal processes*
675 *(denitrification)*

Flux Name	Reference	Flux Value (kt N/yr)	ABS-NO$_3$-N/Flux Value (-)
ABS-NO$_3$-N	This study	24.2	-
Organic N retention by abstraction	Finlay et al. (2016)	3.9	6.21
Organic N storage in floodplains	Finlay et al. (2016)	0.8	30.03
Organic N storage in channel	Finlay et al. (2016)	1.6	15.02
Denitrification in the hydrosphere (rivers, groundwater and coastal marine environments)	Leip et al. (2011); Worrall et al. (2012)	62 -716	0.39 – 0.03

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679 *Table 2 Total flux of nitrate entering the environment from mains water leakage (MWL-NO$_3$-N) in England for 2015 in*
680 *comparison to previous estimates of N sources (MWL-NO$_3$-N, N from leaking sewers, all N sources, urban diffuse N sources).*
681 *MWL-NO$_3$-N/Flux Value refers to the MWL-NO$_3$-N estimate made in this study.*

Flux Name	Reference	Flux Value (kt N/yr)	MWL-NO$_3$-N/Flux Value (-)
MWL-NO$_3$-N	This study	3.62	-
MWL-NO$_3$-N	Environment Agency (2013)	20.31	0.178
SEWER-N	Environment Agency (2013)	4.06	0.891
All N sources	Zhang et al. (2014)	277	0.013
Urban diffuse N sources	Zhang et al. (2014)	2.31	1.567

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