1 Groundwater Quality: Global Threats, Opportunities and Realising the

- 2 **Potential of Groundwater**
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11 Abstract

Groundwater is a critical resource enabling adaptation due to land use change, 12 13 population growth, environmental degradation, and climate change. It can be a driver of change and adaptation, as well as effectively mitigate impacts brought 14 about by a range of human activities. Groundwater quality is key to assessing 15 groundwater resources and we need to improve our understanding and coverage of 16 groundwater quality threats if we are to use groundwater sustainably to not further 17 burden future generations by limiting resources and/or increasing treatment or 18 19 abstraction costs. Good groundwater quality is key to progress on a range of Sustainable Development Goals, but achievement of those goals most affected by 20 21 groundwater contamination is often hindered by of a lack of resources to enable

22 adaptation. A range of threats to groundwater quality exist, both natural and anthropogenic, which may constrain groundwater use. However, groundwater often 23 provides good quality water for a range of purposes and is the most important water 24 resource in many settings. This special issue explores some of the key groundwater 25 quality challenges we face today as well as the opportunities good groundwater 26 quality and treatment solutions bring to enhance safe groundwater use. Legacy 27 28 anthropogenic contaminants and geogenic contaminants may be well documented in certain places, such as N America, Europe and parts of Asia, however, there is a 29 30 real issue of data accessibility in some regions, even for more common contaminants. This paucity of information can restrict our understanding and ability to 31 manage and protect groundwater sources. Compared to surface water quality, large 32 scale assessments for groundwater quality are still scarce and often rely on 33 inadequate data sets. Better access to existing data sets and more research is 34 needed on many groundwater quality threats. Identification and guantification of 35 these threats will support the wise use and protection of this subsurface resource, 36 allow society to adequately address future challenges, and help communities realise 37 the full potential of groundwater. 38

Keywords: Groundwater Quality, Geogenic, Anthropogenic, Adaptation, Water
Security, SDGs

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45 **1. Introduction**

Groundwater is the largest freshwater store on earth, its use underpins a huge range 46 of human activities as well as important ecosystems (Margat and Van der Gun, 47 2013; Rohde et al., 2017). Historically, groundwater quantity has often been the 48 focus of groundwater resource assessments, and there is a real need to now focus 49 more attention towards groundwater quality. There is a direct connection between 50 51 stores of available freshwater provided by groundwater and their status and utility in terms of quality (Gleeson et al., 2020). The excellent quality provided by 52 groundwater in many regions, often reflecting the degree of protection from surface 53 contaminants that groundwater provides, is critical for sustaining agriculture, 54 industry, drinking water services and is fundamental to reaching key Sustainable 55 Development Goals (SDGs), e.g. SDGs 2, 6, 9, 11 (UN 2019). However, there are 56 several natural and human-induced water quality threats to groundwater which may 57 constrain its use and necessitate treatment prior to consumption (WWQA, 2021). 58

The recent World Bank report 'Quality Unknown: The Invisible Water Crisis' 59 (Damania et al., 2019), made almost no mention of groundwater quality nor a clear 60 distinction between the threats affecting surface water and groundwater. This is 61 telling and perhaps exposes two important issues: the lack of visibility of 62 groundwater quality as an important topic and the more limited compilation of 63 groundwater-guality data at a global scale compared to surface-water data (WWQA, 64 65 2021). Working towards a global groundwater guality assessment is important because of the significant pressures placed upon quality by human activities and 66 climate variability. Protection of groundwater resources is necessary for protecting 67 human health, groundwater-dependent livelihoods and ecosystems. Many regions 68

globally rely on naturally clean groundwater as advanced centralised water treatment
is not feasible due to logistics and costs (Howard et al., 2006; Edokpayi et al., 2018;
Khan et al., 2020). Knowing where to source clean groundwater, as well as
understanding threats to this resource, and sustainable treatment solutions is
therefore of paramount importance.

Recent studies assessing the availability of groundwater have begun to consider the 74 75 quality dimension and factor in the potential constraints due to poor water quality (Gleeson et al., 2020). Indeed, in the Indo-Gangetic Basin, the world's most heavily 76 abstracted aguifer system, groundwater guality constraints have been shown to 77 exceed those due to depletions in groundwater stores caused by over-pumping 78 (MacDonald et al., 2016). Deterioration of groundwater guality is a global threat, 79 impacting at a range of scales, from localised point sources of contamination e.g. 80 from septic tanks or pit latrines (e.g. Graham and Polizzotto 2013), to diffuse 81 pollution affecting large aquifer systems e.g. nitrate contamination (Ascott et al., 82 2017) or salinity induced by irrigation (Bouafar and Kuper 2012). Natural 83 groundwater quality may also be compromised, for example geogenic arsenic, 84 fluoride and natural sources of salinity impacts compromise drinking water quality 85 86 use of groundwater for irrigation. Thus, natural groundwater quality needs to be understood and the risks of groundwater development in compromised environments 87 mitigated before development and use (Smedley and Kinniburgh 2002; Edmunds 88 and Smedley 2013; Hug et al., 2020). There are many groundwater guality threats 89 that occur at a global level, underpinned by common geological controls and drivers 90 in land use, land management and stewardship. 91

It is also important to recognize that surface water and groundwater are closely
linked – pollution of one can pollute the other. Worldwide, a large volume of river and
streamflow discharge is sourced from groundwater as baseflow, with many rivers
deriving over half their flow from groundwater sources (Swanson et al 2020; Beck et
al 2013). Particularly vulnerable are springs and wetlands where subsurface
contamination can directly impact groundwater-dependent ecosystems (Springer et
al. 2008; Kreamer et al. 2015).

This special issue provides a unique collection of papers which address some of the 99 water quality challenges we face at a global scale. It covers opportunities that 100 groundwater provides for a range of uses, and covers some treatment and 101 management solutions for several key groundwater guality threats. Groundwater 102 quality threats are varied, this Special Issue covers many of these (e.g. faecal 103 contaminants, salinity, arsenic, fluoride, radionuclides, iron, manganese, pesticides 104 and per- and polyfluoroalkyl substances) but clearly it was beyond the scope of this 105 special issue to deal with all groundwater quality challenges. Indeed, many are 106 107 covered in other recent publications (e.g. Horst et al., 2018; Stockdyk et al., 2020; Wang et al., 2020; Andrade et al., 2020; Podgorski and Berg 2020; Bunting et al., 108 109 2021; Birhanu et al., 2021). This collection provides evidence from large scale studies and some examples from data-scarce regions and emphasises the critical 110 importance of groundwater quality when considering water availability and protection 111 of water sources for future water use. This special issue comes at a time when our 112 focus is drawn towards the importance of groundwater - the UN World Water Day 113 2022 is focussed on "Groundwater: Making the Invisible Visible", and the threats 114 115 from climate change (COP26). The special issue provides a timely reminder of the

groundwater-quality challenges we continue to face as well as the opportunities itcan bring to build resilient and sustainable water supplies today and in the future.

2. Capacity for aquifers to buffer water quality threats

119 One of the core attributes of groundwater is its ability to provide high-quality water 120 which requires limited treatment for drinking water in many cases. This is due to the 121 protective cover provided by the soil as well in cases with deeper unsaturated zones. This means that surficial contamination sources can be attenuated through a 122 123 combination of physical, chemical and biological processes. While the protective properties of groundwater systems can be absent or by-passed in some instances, 124 overall groundwater is much less susceptible to high levels of surface contamination 125 compared to surface waters. This water-quality buffering capacity mirrors the water-126 quantity buffering capacity of groundwater compared to surface sources replenished 127 128 directly by rainfall and runoff.

129 Shallow groundwater systems are evidently more susceptible to surficial contamination threats from anthropogenic sources compared to deeper groundwater 130 systems with much longer residence times (Lapworth et al., 2015, 2013; Banks et al., 131 132 2021). In some cases, geogenic sources of contamination (e.g. As and U) are hosted in surficial and shallow sediments or deposits which limits the use of these more 133 easily accessible aguifers for drinking-water supply and irrigation (Nickson et al., 134 1998; Smedley and Kinniburgh 2002; Van Geen et al., 2006). However, in many 135 settings the water quality of shallow aquifers is highly suited for other uses such as 136 137 industry. This raises the issues of development of deeper groundwater sources which are replenished over much longer timescales (Bethke et al., 1999; Edmunds et 138 al., 2006; Hoque and Burgess 2012). At intermediate depths in many sedimentary 139

basins fresh paleo waters that are present in some regions provide important
sources of drinking water (e.g. Michael and Voss 2009; Burgess et al., 2010). At
greater depths water quality can deteriorate and at the base of many sedimentary
systems flow is often limited and saline groundwaters are found (Ferguson et al.,
2018).

3. Global threats to groundwater quality

There are numerous global treats to groundwater quality, and these can be 146 147 categorised broadly into two groups - those controlled by variations in geogenic contaminants such as arsenic and fluoride, and those introduced by human activities 148 either at the surface or at depth which compromise groundwater quality. Examples 149 include the deterioration of groundwater quality due to over pumping of coastal 150 aquifers (Tam et al., 2014), the mobilisation of buried contaminants due to pumping 151 152 and the influx of fresh sources of organic matter (Lawson et al., 2016) and the stimulation of denitrification due to flooding in alluvial aguifer systems or raised 153 groundwater levels (Bernard-Jannin et al., 2017). 154

Threats to groundwater quality have been researched for many decades, necessitate 155 treatment in some cases and limit water use globally. These include threats from 156 contaminants derived from agricultural activities, e.g. nitrate, plant protection 157 products and co-contaminants of fertilisers such as uranium (Kolpin et al., 1998; 158 Squillace et al., 2002; Liesch et al., 2015; Padilla et al., 2018). Threats from industry 159 and urban settlements, e.g. heavy metals, petroleum based contaminants, selected 160 waste water organics and microbiological contaminants (Lapworth et al., 2012; 161 2017a; Hepburn et al., 2019; Diaw et al., 2020; Steelman et al., 2020). There are 162 also threats from widely occurring geogenic contaminants, e.g. arsenic, fluoride, 163

radionuclides, iron, manganese (Coyte et al., 2018; Johnson et al., 2018; 164 Bhattacharya et al., 2020). High salinity is perhaps one of the most pervasive and 165 166 challenging groundwater quality issues and can arise due to natural sources of salinity as well as anthropogenic sources and drivers of salinity (Micheal et al., 2013; 167 Comte et al., 2016; Thorslund and van Vliet 2020). Many of these water quality 168 threats are the focus of papers within this special issue due to their global footprint. 169 170 While the groups of contaminants described above pose a global threat and are better characterised than other contaminants, there are still many regions for which 171 172 basic information on water-quality parameters such as nitrate and salinity are inaccessible or have not yet been collected. This lack of data and knowledge is in 173 itself a challenge for using and managing groundwater resources effectively. 174

There are also many new groups of contaminants, often referred to as 'emerging 175 contaminants' or 'contaminants of emerging concern' such as per- or polyfluorinated 176 organic compounds, pharmaceuticals, microplastics, nanomaterials and a whole 177 range of organic breakdown products. These new types of threats to groundwater 178 179 clearly have a global footprint, but there is still limited evidence globally with which to understand their occurrence, controls and wider impacts on groundwater quality (Re 180 181 et al., 2019; Lapworth et al., 2019; Panno et al., 2019). This is due to both the costs of analysis for these groups of contaminants, in some cases still developing 182 protocols for sampling and analysis (e.g. microplastics), and the lack of regulatory 183 drivers for the collection of this type of water quality data in groundwater in many 184 regions (Re et al., 2019; Lapworth et al 2019). To date, the focus of many of these 185 emerging contaminants has been in surface-water bodies due to the dominant risk 186 posed by many of these contaminants, but more work clearly needs to be 187

undertaken to improve our understanding of pathways and threats to groundwatersources from these types of contaminants.

The field of microbial contamination in groundwater is arguably still a rapidly 190 progressing research area, particularly for more challenging microbes such as 191 viruses (Stokdyk et al., 2020; Sorensen et al., 2021). The issue of anti-microbial 192 resistance (AMR) is a very active and developing field of research. However, there 193 194 are still only limited studies focussing on groundwater systems as hosts for conditions which enhance AMR including drivers due to complex mixtures of organic 195 contaminants and other stress factors (Andrade et al., 2020). Much like the field of 196 'emerging organic contaminants', recent advances in analytical and data processing 197 capabilities are rapidly advancing our ability to understand biological threats and the 198 complexity of groundwater biomes in more detail. Several contributions in this 199 special issue address these more emerging threats, including microbiological 200 contamination and remediation, and contamination from pharmaceuticals and other 201 202 emerging organic compounds.

4. Opportunities for groundwater development and assessment

204 While there is considerable evidence from many regions globally that overabstraction is depleting groundwater stores (Wada et al., 2010), there are many 205 regions with underutilised groundwater potential (MacDonald et al., 2012; Cobbing 206 and Hiller 2019). There are large humid regions in Africa for example, that have 207 sufficient recharge and groundwater stores to support more abstraction and 208 209 adaptation to climate impacts (MacDonald et al., 2019; 2021). Many of these regions are relatively sparsely populated, have had more limited surficial contaminant loads 210 compared to many other regions (e.g. Europe) with a long legacy of use of synthetic 211

fertilisers and plant protection products, and generally contain groundwaters with 212 good water quality even when drinking-water quality standards are used as the 213 criterion for assessment (Silliman et al., 2007; Anku et al., 2009; Rivett et al., 2018; 214 Lapworth et al., 2013; 2019). Many shallow basement and sedimentary aquifers 215 contain groundwater with low total dissolved solids contents due to the nature of 216 recharge and water-rock interactions and are suitable for irrigation use (e.g. 217 218 Lapworth et al., 2021; 2020; 2017b). However, often assessments of the suitability of groundwater for irrigation ignore groundwater guality (Altchenko and Villholth 2015) 219 220 or only feature once water quality problems are well documented and widespread (e.g. Feng et al., 2005). In basement settings, it is often water quantity and the rate 221 of replenishment that may constrain development of groundwater for a range of uses 222 (MacDonald et al., 2021). While there is a critical role for deeper groundwater 223 resources in settings where shallower sources are contaminated it is important to 224 225 monitor abstraction and changes in water quality to ensure that there is no contaminant breakthrough from shallower aquifers as a result of abstraction or poor 226 borehole construction (Ravenscroft et al., 2018; Lapworth et al., 2018a, 2018b). 227

A range of Managed Aquifer Recharge (MAR) schemes exist at different scales 228 229 which can potentially enhance groundwater recharge and quality locally. Many schemes have taken water quality considerations into account, either through the 230 use of the unsaturated zone or though pre-treatment technologies prior to injection or 231 infiltration into aquifers. However, where this has not been factored in or where there 232 is opportunity for rapid by-pass flow it is possible that groundwater quality may be 233 compromised under such schemes – this is a particular risk for direct injection 234 schemes (Dillon et al., 2020a). MAR may in some circumstances promote the 235 improvement of groundwater quality (Dillion et al., 2020b) through changes in redox 236

conditions and subsequent denitrification or sorption of contaminants, or throughdilution in regions impacted by salinity.

Groundwater of varying natural quality can be used for different purposes, for 239 example industry, aquaculture, irrigation and livestock all have different water quality 240 considerations. As such, there may be opportunities to exploit groundwater for 241 livelihoods even if it is not suitable for human consumption without prior treatment. A 242 243 wide range of existing and new technologies (e.g. filtration methods, osmosis, new membrane technology and the use of nanotechnology) to improve water quality and 244 remove or reduce bacteria, arsenic, fluoride, iron and salinity, to name a few 245 examples are available (WHO 2009; Boving et al., submitted; Richards et al., 246 submitted). These new technologies represent an opportunity to increase the use of 247 groundwater and develop new groundwater resources and is the topic of some of the 248 contributions to this special issue. 249

The use of machine learning and other statistical methods have, in some cases, 250 enabled regional- or global-large-scale assessments to be made, but these are still 251 252 constrained by the availability of reliable observations and the use of proxy input data sets (Podgorski et al., 2018; 2020). The use of sensors can also improve our 253 understanding of particular threats to groundwater quality and may enable more 254 high-resolution data (in both space and time) to be gathered rapidly for selected 255 parameters such as nitrate, salinity (e.g. Dulaiova et al., 2010; Opsahl et al., 2017) 256 257 and threats from faecal contamination (e.g. Sorensen et al., 2016; Ward et al., 2020). However, there is still a fundamental issue of poor coverage of groundwater-quality 258 data and limited availability in many regions (much of Africa, parts of Asia and S 259 260 America), as well as data bias in certain regions and for certain parameters (e.g. S

Asia for arsenic and parts of Europe and N America for many parameters), which limit assessments undertaken at scales comparable to those for rivers and lakes.

263 **4. Concluding remarks and future outlook**

264 Groundwater quality treats arise due to due to human activities and due to naturally 265 occurring geogenic sources of contamination. Anthropogenic activities can also both enhance and mitigate threats to groundwater quality. Groundwater should also be 266 recognised as an opportunity and underutilised resource in some settings with 267 268 enormous adaptive potential. The recent World Bank assessment of global water guality (Damania et al., 2019) highlights the critical need for more emphasis on 269 groundwater quality as an important aspect of water resource assessment. It also 270 demonstrated the limited visibility of both global groundwater quality threats and 271 opportunities. Very few studies have been able to make truly 'global' assessments of 272 273 groundwater quality (e.g. Ascott et al., 2017; McDonough et al., 2020; Thorslund and van Vilet 2020; Podgorski and Berg, 2020) and for those which have, there are 274 clearly large data gaps for many regions. There is an urgent need to improve data 275 276 coverage in some regions such as Africa and parts of Asia and South America and to coordinate initiatives focussed on making data more accessible (WWQA 2021). 277

Good groundwater quality underpins progress on a range of Sustainable
Development Goals and can provide safe and resilient water supplies, able to buffer
changes in climate extremes as well as other anthropogenic pressures such as landuse change. The adage 'you can only manage what you know' is true in many
senses regarding groundwater quality. It is probably fair to say that while there has
been massive progress in the last three decades on the understanding of

groundwater quality threats, their complexities, as well as the opportunitiesgroundwater quality brings, a great deal remains to be done on this topic.

There are many potential threats to groundwater quality that we are aware of and 286 which are well understood, and other 'emerging threats' that we are only just starting 287 to investigate. There continue to be rapid advances in analytical techniques, 288 statistical methods and treatment technology which will, over the coming years 289 290 broaden our understanding of groundwater threats and also provide potential solutions. Large stores of shallow groundwater with water quality suitable for a range 291 of uses still have the potential to be utilised, these include humid regions with high 292 annual recharge, as well as less humid and more water-scarce regions where 293 groundwater is the only reliable source of water (MacDonald et al., 2021). However, 294 water quality and quantity assessments are rarely undertaken in parallel to allow a 295 more complete assessment of water security, and this is clearly an area where 296 improvements can be made. The quality of groundwater is key to assessing 297 groundwater resources at a range of scales from local to global and this assessment 298 299 needs to be improved if we are to realise their potential.

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