Supplementary Material

Surface water and groundwater quality in South Africa and Mozambique – Analysis of the most critical pollutants for drinking purposes and challenges in water treatment selection.

Paola Verlicchi*, Vittoria Grillini

- Department of Engineering, University of Ferrara, Via Saragat 1, 44122 Ferrara, Italy <u>paola.verlicchi@unife.it;</u> vittoria.grillini@unife.it
- * Correspondence: paola.verlicchi@unife.it; +39 (0)532.974938

Table S1. Average per capita water requirements for different categories of settlements [1,2]

Category of settlement	L/(per capita day)
Medium-sized towns	150-200
Small towns (included water needs for animals and small gardens)	200-250
Coastal towns (permanent visitors)	200-250
Coastal towns (seasonal visitors)	80-130
Rural village	60-100
Farm village (includes water needs for animals and small gardens)	100-150

References for Table S1

[1] DWA. Department of Water Affairs, South Africa 2009. Development of Reconciliation Strategies for all Towns in the Southern Planning Region: Inception Report. Prepared by Umvoto Africa (Pty) Ltd in association with Aurecon (Pty) Ltd on behalf of the Directorate: National Water Resource Planning. Department of Water Affairs, Pretoria, South Africa

[2] Hay, E.R.; Riemann, K.; van Zyl, G.; Thompson, I. Ensuring water supply for all towns and villages in the eastern cape and western cape provinces of South Africa. *Water SA* **2012**, *38(3)*, 437-44, doi.org/10.4314/wsa.v38i3.9.

Table S2. Main characteristics of the sampling pounts in the peer reviewed papers included in this study.

Paper	Area Type: Rural (R), Peri-urban (PU)	Study site: details
Abia et al., 2015	PU	Water samples were taken in different points from the Apies River, in the Gauteng Province, South Africa and analyzed for <i>Escherichia coli</i> . Samples were taken in the area where the river is used for fishing, irrigation, as a water source for flocks, also for disposal of wastes of the surrounding villages
Abiye and Bhattacharya 2019	R	20 groundwater samples were taken in the area of Namaqualand in the Northern Cape Province and analyzed for 9 metals including As. This area is characterized by a lack of rainfall, climatic aridity and absence of surface water. Local communities rely on groundwater resources for their uses.
Abiye and Leshomo, 2013	R	The study site corresponds to Namaqualand in Northern Cape province. It's a rural area. 57 water samples were collected from boreholes currently used for human and animal consumption for the determination of physico-chemical parameters, inorganic constituents, stable isotopes and trace metals.
Abiye and Leshomo, 2014	R	The study site corresponds to Namaqualand in Northern Cape Province. It's a rural area. 30 water samples were collected from boreholes for major ion and metal determination
Abiye et al., 2018	R	Samples were collected from the Waterberg thermal fields (Limpopo) and the Namaqualand region (South Africa)for the determination of geochemical paramters as well as fluoride.
Agunbiade and Moodley, 2014	PU- R	Samples were taken from the Umgeni River (257 km from the source to the release in the Indian Ocean), KwaZulu-Natal province, South Africa. Sampling campaigns included 7 points in the dam region corresponding to a peri-urban -rural area for the determination of 17 pharmaceuticals.
Agunbiade and Moodley, 2016	PU-R	Samples included in the current review were taken from surface water (Msunduzi River in KwaZulu-Natal Province, South Africa) and were analyzed for a selection of pharmaceuticals.
Archer et al.,2017	PU	Sampling points in surface water are not reported in details
Barbieri et al., 2019	R	25 groundwater and surface water samples were taken in the area of Limpopo Natinal Park, Gaza province, Southern Mozambique and analyzed for main chemical and physical parameters, ions. The aim of the paper is to evakuate if these sampled resources could be adequate for human consumption and irrigation
Bezuidenhout et al., 2002	R	Water samples were taken from the Mhlathuze River in KwaZulu-Natal (RSA) and analyzed for microbiological and physical-chemical parameters. The sampled area is a typical rural area in this region.
Chilundo et al.,2008	R	Water samples were taken along the Limpopo River in Mozambique in order to collect data for establishing a water quality monitoring network.
Dzoma et al., 2010	R, PU	Samples were taken from stream water in a mining area near Orkney, in the North West Province of South Africa
Edokpayi et al., 2014	R, PU	Samples were taken from Dzindi River, in the Limpopo Province, South Africa and analyzed for chemical and physical parameters, heavy metals
Edokpayi et al., 2015	R	Samples were taken from Mvudi River, South Africa, and analyzed for chemical and physical properties, selected ions, microbiological parameters. The study area includes formal and informal settlements.

Edokpayi et al., 2016a	R	36 samples were taken from the Mvudi River, South Africa, and analyzed for trace metal concentrations over the year.
Edokpayi et al., 2016b	R and PU	Water samples were taken from Mvudi River and Nzhelele River n Vhembe District, South Africa and analyzed for Polycyclic Aromatic Hydrocarbons (PAHs) (
Edokpayi et al., 2017	R	36 water samples were taken from Nzhelele River and analyzed for trace metals.
Edokpayi et al., 2018	R and PU	24 groundwater samples were taken from 8 boreholes in Muledane area in the Limpopo Province in South Africa and analyzed for heavy metals
Fatoki et al., 2001	PU	Samples were taken from Umtata River, Eastern Cape in a peri-urban catchment area and analyzed for turbidity, microbiological and cadmium pollution.
Fatoki et al., 2002	PU	Samples were taken from Umtata River, Eastern Cape in a peri-urban catchment area and analyzed for dissolved trace metals.
Fatoki et al., 2003	PU	Samples were taken from Umtata, Buffalo, Keiskamma and Tyume Rivers and in the Sandile and Umtata Dams in the eastern Cape province, South Africa. They were analyzed for Cd, Hg and Zn.
Fatoki et al., 2004	PU and R	Samples were taken from the Umtata River in a periurban and rural area and were analyzed for cadmium in order to evaluate the level of health risk to communities along the river banks who rely on it as their primary domestic source.
Gumbi et al., 2017	PU	Water samples were taken from Umgeni river, Kwa-Zulu Natal Province, in different sampling points in periurban areas and analyzed for pharmaceuticals.
Jackson et al., 2007	PU and R	Samples were taken from the catchment area of Berg River: in an agricultural farming area and in the informal settlement of Mbekweni (Western Cape, South Africa). They were analyzed for trace metals.
Jackson et al., 2009	PU	Samples were taken from two rivers in the Western Cape south Africa and analyzed for trace metals
Leusch et al., 2018	PU	Water samples were taken from a dam/lake in a nature reserve in Gauteng <province, africa="" analyzed="" and="" for="" pharmaceuticals<="" some="" south="" td=""></province,>
Lin et al., 2004	R	Samples were taken from Mhlathuze River, Kwa-Zulu Natal, RSA) and analyzed for chemical, physical and microbiological parameters.
Madikizela and Chimika, 2017	PU and R	Water samples were taken from Mbokodweni river, South Africa and analized for naproxen, diclofenac and ibuprofen.
Madikizela et al., 2014	PU and R	Water samples were taken from Mbokodweni river, South Africa and analized for triclosan and ketoprofen
Manickum and John 2014	PU	Water samples were taken from Umsunduzi River and aanalized for endocrine disrupting compounds.
Matongo et al., 2015a	PU	Samples were taken in different sampling point along Umgeni River, KwaZulu-Natal, RSA in order to evaluate the occurrence of a selection of pharmaceuticals
Matongo et al., 2015b	PU and R	Water smples were taken in different sampling point along Msunduzi River, KwaZulu-Natal, RSA and analyzed for a selection of phramceuticals
Nekhavhambe et al. 2014	R and PU	Water samples were taken from different rivers around Thohoyandou, Limpopo Province, RSA and analyzed for PAHs
Obi et al., 2002	R	Samples were taken from the river water sources in the rural Venda communities, Northern Province, South Africa, and analyzed for microbial indicators.
Odiyo and Makungo, 2012	R	Water samples were taken from groundwater in Siloam Village, Limpopo Province, South Africa and analyzed for fluoride concentrations. This village is a typical rural village in South Africa with high fluoride concentrations, the likely sources of fluoride, the factors afecting concentrations and the impact on human health

Odiyo and Makungo,	R	Water sample were taken from 11 boreholes in Siloam Village, Limpopo Province and analyzed for chemical and physical parameters
2018		as well as microbial indicators in order to evaluate the contamination level of boreholes used for domestic use in the rural village.
Olatunji et al., 2017	PU	Water samples were taken from surface water in a river receiving untreated farm wastewater and analyzed for steroid hormones
Rimayi et al., 2018	PU	Samples were taken from the Hartbeespoort Dam, Gauteng Province, Soth Africa and analized for pharmaceuticals and antivirals.
Segura et al., 2015	PU and R	Water samples were taken from surface water in RSA and Mozambique and analyzed for antinfectives.
Sibanda et al., 2013	R	Samples were taken from the Tyume River in the Eastern Cape Province of South Africa and analyzed for microbiological parameters
Van Wyk and Coetzee,	R	Groundwater samples were taken from boreholes in the Bushmanland and Namaqualand areas, Northern Cape Province, South
2008		Africa and analyzed for uranium
Wanda et al., 2017	PU	Samples were taken from groundwater and surface water in Gauteng, Mpumalanga and North West and analyzed for emerging micropollutants.
Wood et al., 2015	PU	Samples were taken from different surface water points in Western cape, KwaZulu- Natal, Freee, Limpopo, Northern Cape provinces, South Africa and analized for anti-virals
Wooding et al., 2017	PU	Samples were taken from surface water in Rietvelei Nature Reserve (Pretoria) and Albasini Dam (Limpopo Province), South Africa and analyzed for anti-virals.

References for Table S2

- Abia, A. L. K.; Ubomba-Jaswa, E.; Momba, M. N. B. Impact of seasonal variation on *Escherichia coli* concentrations in the riverbed sediments in the Apies River, South Africa. *Sci. Total Environ.* 2015, 537, 462–469, doi:10.1016/j.scitotenv.2015.07.132.
- 2. Abiye, T. A, Bybee, G., Leshomo, J. Fluoride concentrations in the arid Namaqualand and the Waterberg groundwater, South Africa: 45. Understanding the controls of mobilization through hydrogeochemical and environmental isotopic approaches. *Groundwater for Sustainable Development* **2018**, *6*, 112–120, doi:10.1016/j.gsd.2017.12.004.
- 3. Abiye, T. A.; Bhattacharya, P. Arsenic concentration in groundwater: Archetypal study from South Africa. Groundwater for Sustainable Development 2019, 9. doi:10.1016/j.gsd.2019.100246.
- 4. Abiye, T. A.; Leshomo, J. T. Groundwater flow and radioactivity in Namaqualand, South Africa. Environ. Earth Sci. 2013, 70(1), 281–293, doi:10.1007/s12665-012-2126-9.
- 5. Abiye, T.A; Leshomo, J. Metal enrichment in the groundwater of the arid environment in South Africa. Environ. Earth Sci. 2014, 72(11), 4587-4598, doi:10.1007/s12665-014-3356-9.
- 6. Agunbiade, F. O.; Moodley, B. Occurrence and distribution pattern of acidic pharmaceuticals in surface water, wastewater, and sediment of the Msunduzi River, Kwazulu-Natal, South Africa. *Environ. Toxicol. Chem* **2016**, *35*(1), 36–46. doi:10.1002/etc.3144.
- 7. Agunbiade, F. O.; Moodley, B. Pharmaceuticals as emerging organic contaminants in Umgeni river water system, KwaZulu-natal, South Africa. *Environ. Monit. Assess.* 2014, *186*(11), 7273–7291. doi:10.1007/s10661-014-3926-z.
- 8. Archer, E.; Petrie, B.; Kasprzyk-Hordern, B.; Wolfaardt, G. M. The fate of pharmaceuticals and personal care products (PPCPs), endocrine disrupting contaminants (EDCs), metabolites and illicit drugs in a WWTW and environmental waters. *Chemosphere* 2017, *174*, 437–446. doi:10.1016/j.chemosphere.2017.01.101.
- 9. Barbieri, M.; Ricolfi, L.; Vitale, S.; Muteto, P. V.; Nigro, A.; Sappa, G. Assessment of groundwater quality in the buffer zone of Limpopo National Park, Gaza Province, Southern Mozambique. *Environ. Sci. Pollut. Res.* 2019, *26(1)*, 62–77, doi:10.1007/s11356-018-3474-0.
- 10. Bezuidenhout, C. C.; Mthembu, N.; Puckree, T.; Lin, J. Microbiological evaluation of the Mhlathuze river, KwaZulu-natal (RSA). Water SA 2002, 28(3), 281-286, doi:10.4314/wsa.v28i3.4895.
- 11. Chilundo, M.; Kelderman, P.; Ókeeffe, J. H. Design of a water quality monitoring network for the Limpopo river basin in Mozambique. *Phys. Chem. Earth* 2008, 33(8-13), 655-665, doi:10.1016/j.pce.2008.06.055.
- 12. Dzoma, B. M.; Moralo, R. A.; Motsei, L. E.; Ndou, R. V.; Bakunzi, F. R. Preliminary findings on the levels of five heavy metals in water, sediments, grass and various specimens from cattle grazing and watering in potentially heavy metal polluted areas of the north west Province of South Africa. J Anim. Vet. Adv. 2010, 9(24), 3026–3033. doi:10.3923/javaa.2010.3026.3033.

- 13. Edokpayi, J. N.; Enitan, A. M.; Mutileni, N.; Odiyo, J. O. Evaluation of water quality and human risk assessment due to heavy metals in groundwater around Muledane area of Vhembe district, Limpopo Province, South Africa. *Chem. Cent. J.* 2018, *12(1)*. doi:10.1186/s13065-017-0369-y.
- 14. Edokpayi, J. N.; Odiyo, J. O.; Msagati, T. A. M.; Potgieter, N. Temporal variations in physico-chemical and microbiological characteristics of Mvudi river, South Africa. Int. J. Environ. Res. Public Health 2015, 12(4), 4128-4140, doi:10.3390/ijerph120404128.
- 15. Edokpayi, J. N.; Odiyo, J. O.; Olasoji, S. O. Assessment of heavy metal contamination of Dzindi River, in Limpopo Province, South Africa. Int. J. Nat. Sci. Res. 2014, 2(10), 185–194.
- Edokpayi, J. N.; Odiyo, J. O.; Popoola, O. E.; Msagati, T. A. M. Assessment of trace metals contamination of surface water and sediment: A case study of Mvudi river, South Africa. Sustainability 2016, 8(2), doi:10.3390/su8020135.
- 17. Edokpayi, J. N.; Odiyo, J. O.; Popoola, O. E.; Msagati, T. A. M. Evaluation of temporary seasonal variation of heavy metals and their potential ecological risk in Nzhelele river, South Africa. *Open Chem.* 2017, *15(1)*, 272–282, doi:10.1515/chem-2017-0033.
- Edokpayi, J. N.; Odiyo, J. O.; Popoola, O. E.; Msagati, T. A. M. Determination and distribution of polycyclic aromatic hydrocarbons in rivers, sediments and wastewater effluents in Vhembe district, South Africa. Int. J. Environ. Res. Public Health 2016, 13(4), doi:10.3390/ijerph13040387.
- 19. Fatoki, O. S.; Awofolu, O. R.; Genthe, B. Cadmium in the Umtata river and the associated health impact on rural communities who are primary users of water from the river. *Water SA* 2004, *30(4)*, 507–513. doi:10.4314/wsa.v30i4.5103.
- 20. Fatoki, O. S.; Awofolu, R. Levels of Cd, Hg and Zn in some surface waters from the Eastern Cape Province, South Africa. Water SA 2003, 29(4), 375-380, doi:10.4314/wsa.v29i4.5042.
- 21. Fatoki, O. S.; Lujiza, N.; Ogunfowokan, A. O. Trace metal pollution in Umtata river. Water SA 2002, 28(2), 183-189, doi:10.4314/wsa.v28i2.5160.
- 22. Fatoki, O. S.; Muyima, N. Y. O.; Lujiza, N. Situation analysis of water quality in the Umtata river catchment. Water SA 2001, 27(4), 467-473, doi:10.4314/wsa.v27i4.4959.
- 23. Gumbi, B. P.; Moodley, B.; Birungi, G.; Ndungu, P. G. Detection and quantification of acidic drug residues in South African surface water using gas chromatography-mass spectrometry. *Chemosphere* 2017, *168*, 1042–1050. doi:10.1016/j.chemosphere.2016.10.105.
- 24. Jackson, V. A.; Paulse, A. N.; Odendaal, J. P.; Khan, W. Investigation into the metal contamination of the Plankenburg and Diep rivers, Western Cape, South Africa. *Water SA* 2009, 35(3), 289–300, doi:10.4314/wsa.v35i3.76766.
- 25. Jackson, V. A.; Paulse, A. N.; Van Stormbroek, T.; Odendaal, J. P.; Khan, W. Investigation into metal contamination of the Berg river, Western Cape, South Africa. *Water SA* 2007, 33(2), 175–182, doi:10.4314/wsa.v33i2.49057.
- 26. Leusch, F. D. L.; Neale, P. A.; Arnal, C.; Aneck-Hahn, N. H.; Balaguer, P.; Bruchet, A.; Escher, B.I.; Esperanza, M.; Grimaldi, M.; Leroy, G.; Scheurer, M.; Schlichting, R.; Schriks, M.; Hebert, A.; Analysis of endocrine activity in drinking water, surface water and treated wastewater from six countries. *Water Res.* **2018**, *139*, 10–18. doi:10.1016/j.watres.2018.03.056.
- 27. Lin, J.; Biyela, P. T.; Puckree, T.; Bezuidenhout, C. C. A study of the water quality of the Mhlathuze river, KwaZulu-natal (RSA): Microbial and physico-chemical factors. *Water SA* 2004, 30(1), 17–22, doi:10.4314/wsa.v30i1.5021.
- 28. Madikizela, L. M.; Chimuka, L. Occurrence of naproxen, ibuprofen, and diclofenac residues in wastewater and river water of KwaZulu-Natal Province in South Africa. *Environ. Monit. Assess.* 2017, 189(7). doi:10.1007/s10661-017-6069-1.
- 29. Madikizela, L. M.; Muthwa, S. F.; Chimuka, L. Determination of triclosan and ketoprofen in river water and wastewater by solid phase extraction and high performance liquid chromatography. S. Afr. J. Chem. 2014, 67, 143–150.
- 30. Manickum, T.; John, W. Occurrence, fate and environmental risk assessment of endocrine disrupting compounds at the wastewater treatment works in Pietermaritzburg (South Africa). *Sci. Total Environ.* **2014**, *468–469*, 584–597. doi:10.1016/j.scitotenv.2013.08.041.
- 31. Matongo, S.; Birungi, G.; Moodley, B.; Ndungu, P. Occurrence of selected pharmaceuticals in water and sediment of Umgeni River, KwaZulu-natal, South Africa. *Environ. Sci. Pollut. Res.* 2015, 22(13), 10298–10308. doi:10.1007/s11356-015-4217-0.
- 32. Matongo, S.; Birungi, G.; Moodley, B.; Ndungu, P. Pharmaceutical residues in water and sediment of Msunduzi River, KwaZulu-Natal, South Africa. *Chemosphere* 2015, *134*, 133-140. doi:10.1016/j.chemosphere.2015.03.093.
- 33. Nekhavhambe, T. J.; van Ree, T.; Fatoki, O. S. Determination and distribution of polycyclic aromatic hydrocarbons in rivers, surface runoff, and sediments in and around Thohoyandou, Limpopo Province, South Africa. *Water SA* 2014, 40(3), 415-424, doi:10.4314/wsa.v40i3.4.

- 34. Obi, C. L.; Potgieter, N.; Bessong, P. O.; Matsaung, G. Assessment of the microbial quality of river water sources in rural Venda communities in South Africa. *Water SA* 2002, 28(3), 287–292, doi:10.4314/wsa.v28i3.4896.
- 35. Odiyo, J. O.; Makungo, R. Chemical and microbial quality of groundwater in Siloam village, implications to human health and sources of contamination. *Int. J. Environ. Res. Public Health* **2018**, *15(2)*. doi:10.3390/ijerph15020317.
- 36. Odiyo, J. O.; Makungo, R. Fluoride concentrations in groundwater and impact on human health in Siloam Village, Limpopo Province, South Africa. *Water SA* 2012, 38(5), 731-736, doi:10.4314/wsa.v38i5.12.
- 37. Olatunji, O. S.; Fatoki, O. S.; Opeolu, B. O., Ximba, B. J.; Chitongo, R. Determination of selected steroid hormones in some surface water around animal farms in Cape Town using HPLC-DAD. *Environ. Monit. Assess.* 2017, *189*(7) doi:10.1007/s10661-017-6070-8.
- 38. Rimayi, C.; Odusanya, D.; Weiss, J. M.; de Boer, J.; Chimuka, L. Contaminants of emerging concern in the Hartbeespoort Dam catchment and the Umgeni River estuary 2016 pollution incident, South Africa Sci. Total Environ. 2018, 627, 1008–1017. doi:10.1016/j.scitotenv.2018.01.263.
- 39. Segura, P. A.; Takada, H.; Correa, J. A.; El Saadi, K.; Koike, T.; Onwona-Agyeman, S.; Ofosu-Anim, J.; Sabi, E.B.; Wasonga, O.V.; Mghalu, J.M.; dos Santos, A.M.; Newman, B.; Weerts, S.; Yargeau, V. Global occurrence of anti-infectives in contaminated surface waters: Impact of income inequality between countries. *Environ. Int.* 2015, *80*, 89–97. doi:10.1016/j.envint.2015.04.001.
- 40. Sibanda, T.; Chigor, V. N.; Okoh, A. I. Seasonal and spatio-temporal distribution of faecal-indicator bacteria in Tyume river in the Eastern Cape Province, South Africa. *Environ. Monit. Assess.* 2013, *185(8)*, 6579–6590, doi:10.1007/s10661-012-3048-4.
- 41. Van Wyk, N.; Coetzee, H. The distribution of uranium in groundwater in the Bushmanland and Namaqualand areas, Northern Cape Province, South Africa. In *Uranium, Mining and Hydrogeology Paper*; Merkel, B.J., Hasche-Berger, A., Eds; Springer: Berlin, Heidelberg, Germany, **2008**; 639–644. ISBN 978-3-540-87745-5.
- 42. Wanda, E. M. M.; Nyoni, H.; Mamba, B. B.; Msagati, T. A. M. Occurrence of emerging micropollutants in water systems in Gauteng, Mpumalanga, and North West Provinces, South Africa. *Int. J. Environ. Res. Public Health* **2017**, *14*(1). doi:10.3390/ijerph14010079.
- 43. Wood, T. P., Duvenage, C. S. J., Rohwer, E. (2015). The occurrence of anti-retroviral compounds used for HIV treatment in South African surface water. *Environ. Pollut.* 2015, 199, 235-243. doi:10.1016/j.envpol.2015.01.030.
- Wooding, M.; Rohwer, E. R.; Naudé, Y. Determination of endocrine disrupting chemicals and antiretroviral compounds in surface water: A disposable sorptive sampler with comprehensive gas chromatography-time-of-flight mass spectrometry and large volume injection with ultra-high performance liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 2017, 1496, 122–132. doi:10.1016/j.chroma.2017.03.057.