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Development of a sampling protocol for radioactive elements in fractured rock aquifers using a case study from South Africa

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This work outlines the methodology employed in order to develop a sampling protocol for radioactive elements in fractured rock aquifers. This has included the analysis of previously developed sampling protocols, historical data as well as the field application of a draft protocol to the area around Beaufort West in South Africa. The selected test site is showcased and the developed protocol is outlined in order to better understand the application of sampling in fractured rock aquifers. This includes the pre-sampling procedures, purging of the well, sampling devices, *in situ* methodologies as well as sampling frequency. Furthermore, the Theory of Sampling applied to a study of this nature is outlined in order to properly contextualise the work. Thereafter, the future outlook for improvements related to this specific protocol is highlighted within the context of Theory of Sampling.

Introduction

Water resources are of the utmost importance due to the fact that water is required in order to aid in the effective functioning of our daily lives. Groundwater resources are very important, because they constitute the larger percentage of the total available fresh water resources.[1] Therefore, studies related to the preservation and judicious use of groundwater resources are critical.

Groundwater can be defined as the water contained in the pore spaces below the surface, excluding the soil moisture in the unsaturated zone.[2] The media within which groundwater occurs could either be of primary porosity, like sand, or of secondary porosity. The latter is due to the fracturing of consolidated sediments. We thus find that fractures occur and these, as well as the rock matrix, are able to store groundwater.[3]

The fractured rock environment underlying the South African landscape has been extensively studied by Woodford and Chevallier.[4] The authors have compiled all the work related to the hydrogeology, geology, remote sensing and water chemistry completed in the South African section of the Karoo. The numerical treatment of the physical parameters of these aquifers can be seen in Botha and Cloot.[5] This includes the rock mechanics as well as applied models to groundwater flow in fractured rock. The determination of Karoo aquifer parameters has further been analysed by Bredenkamp *et al.*[6] and Van Tonder *et al.*[7] These studies have all focused on the geological and hydraulic parameters of these fractured rock aquifers.

The need has arisen for an in-depth understanding of the groundwater geochemistry of these aforementioned aquifers, specifically in areas of limited water supply. This will aid in understanding water quality and in turn help in effective water resource management and allocation.

It is with this in mind that the Water Research Commission decided to fund a study related to Uranium and radioactivity in groundwater in the region of Beaufort West, South Africa. One of the products developed from this study included a sampling and monitoring protocol for radioactive elements in fractured rock aquifers. This document is the first of its kind developed globally and is outlined in brief.

Background

In recent times various studies have characterised the extent to which natural radioactive contamination is occurring within groundwater.[8–10] Unfortunately there seems to be no standard sampling and monitoring protocol for radionuclides within secondary aquifers.[11] A document of this nature is important due to the fact that a major part of South Africa is underlain by hard rock aquifers and they supply numerous towns with potable water for various uses.[12]

It is also important to note that Uranium and its daughter products have adverse effects on human health. This is due to the radioactive nature of the parent material as well as the decay products released over time, more commonly known as daughter products. In order to minimise these impacts the sampling and monitoring of these radionuclides has to be done in an effective standardised manner.

Weaver *et al.*[13] suggests that groundwater sampling is done for the following reasons:

- Assess groundwater quality for fitness of use
- Understanding hydrogeology of an aquifer
- Investigating groundwater pollution
- Water quality monitoring

These reasons are all important and thus the development of a protocol in order to provide a methodology for radioactivity sampling in fractured rock aquifers is just as critical.

Methodology

The methodology used in order to develop the sampling and monitoring protocol presented in Xu *et al.*[14] is outlined in this section. The abridged work presented highlights of the salient points of the developed protocol. An in-depth analysis and presentation of the work can be viewed in the aforementioned literature.

Historical data sets

These data sets aided greatly in understanding applicable methodologies for sampling radioactivity in fractured rock aquifers. The methods used to generate this historic data also contributed towards the development of the protocol. Brunke[15] conducted the initial work relating to the groundwater geochemistry within the vicinity of the

Uranium channels of Beaufort West. The aim of the study was to investigate the possible relationship between Uranium and other trace elements in groundwater in the region. Brunke[15] suggested that the water quality is mainly a function of residence time and extent of rock/water interaction. It was further observed that waters with higher salinity values were enriched in SO_4 and Cl. The sub-surface waters were generally well aerated and had a positive Eh. These conditions favoured the leaching of Uranium, which also had a positive correlation with Total Dissolved Solids (TDS).

Scholtz[16] assessed the potential toxic influence of Uranium trail mining in the Karoo Uranium Province. The study revealed localised elevated values for U, Mo, Pb, Cu, As and Fe in surface- and groundwater, soils, sediment and crops. Scholtz[16] concluded that the U concentration in the groundwater was acceptable. Unfortunately the author did not purge the wells and thus sampled stagnant groundwater. Purging can be seen as the removal of stagnant water from the well. Purging is essential in order to gain a sample which is representative of the *in situ* conditions, especially in fractured rock aquifers.[3]

Sami and Druzynski[17] looked at the predicted spatial distribution of Uranium, Arsenic and Selenium within the borders of South Africa. This report yielded numerous maps for the occurrences of the aforementioned elements in groundwater throughout the country, including the proposed study area. The authors also extensively examined the health hazards, geology, physico–chemical properties as well as sources of Uranium. This is an excellent study, which outlines the theoretical aspects of Uranium migration in the sub-surface as well as deposition of the aforementioned elements. Thereafter, we have thoroughly examined all the aforementioned data relating to the occurrence of radioactivity within the Karoo. We have concluded that the overall water quality is poor, with most of the datasets showing TDS concentrations above the allowable limit of 450 mg L^{-1}. Despite this fact it has been shown, by means of historic data sets, that the levels of Uranium in the groundwater were generally acceptable.

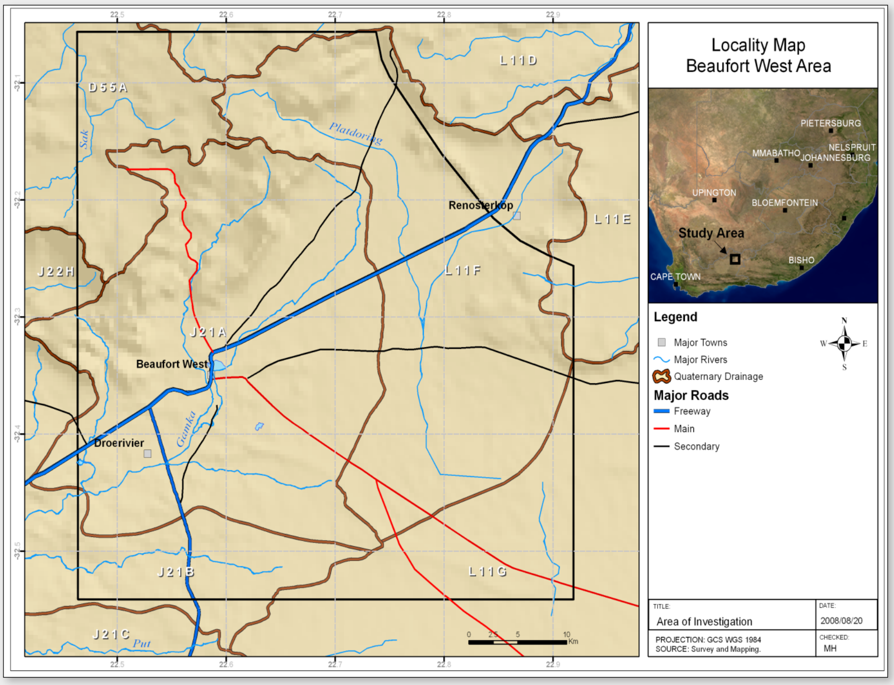

Figure 1. The study area, which is in the vicinity of the Karoo town of Beaufort West.

Field work design

Previous reports as well as maps of the area were consulted in order to determine the boundaries of the study area (Figure 1). The geology and hydrogeology were carefully examined to properly understand groundwater flow. Lastly, boreholes in the vicinity of known Uranium deposits were earmarked for radioactivity sampling.

Sampling

The sites, which are located within the vicinity of the town of Beaufort West, were visited in order to carry out a groundwater sampling exercise. The proposed methodology for sampling radioactive elements was in line with that of heavy metals, as shown below.[13]

The samples were filtered through 0.45 µm filter paper and placed in HDPE sample bottles. The sample which was to be analysed for heavy metals was filtered into a 250-mL plastic bottle and spiked with 10% HNO_3, in order to prevent the heavy metals from precipitating. The radioactive sample, which was filtered into a 5-litre bottle, was also spiked with 10% HNO_3. These radioactive samples were then placed in a cooler box and promptly sent to the laboratory at NECSA for analysis.

In the case of windmills, the sample was taken as close to the outlet pipe as possible. Furthermore, it was assumed that the hole was purged due to the fact that the wind powered pump ran the whole day. With the pumps on the other hand, we find that they are permanently installed, thus making it difficult to determine the depth of the hole as well as the static water level. Therefore, these pumps were allowed to run for a few minutes before being sampled. In many cases the pumps were run prior to the arrival of the team on-site.

Protocol development

Prior to venturing into the field for sampling, a draft sampling protocol was developed in order fully to understand processes and applications which should be implemented for sampling. This process was completed by assessing all the best practices from across the globe, as well as in South Africa, and outlining possible options.

Upon returning from the field, an entire new outlook was required due to the fact that certain applications were not suited for local conditions. Therefore, the protocol was re-evaluated and then refined in order to be more locally applicable and relevant.

Study area

The study area is located in the vicinity of the town of Beaufort West (Figure 1), which lies at approximately 930 m above sea level.[18] At this altitude the majority of the precipitation occurs during the summer months due to a high pressure system dominating the inflow of moisture-filled air into the escarpment.[19] Average precipitation in the vicinity of the town is 235 mm per annum.[20]

The area itself is fairly flat with scattered mesa's and butte's predominating as one draws closer to the Nuweveld mountains in the north, which basically controls groundwater recharge in the area. The major bush types populating the barren soils have been classified by Acocks[21] as being False Karoo and Karroid Bushveld. Furthermore, cattle farming seems to be the dominant agricultural activity with sheep and cows being the major livestock. Satellite imagery has also shown that certain plots of land are also being cultivated along the Gamka, Hans and Kwagga rivers to the south of Beaufort West. The Game reserve, which is located in close proximity to the town, also houses varieties of buck and wildlife.

Hydrogeology

Woodford and Chevallier[4] have extensively examined the hydrogeology in the vicinity of the study area, on a macro scale by means of GIS. The remote sensing methods used to map the dolerite dykes has shown the extent to which these structures impact the landscape. The dykes and sills are major geological features caused by the upwelling of magma. The magma in turn solidifies and causes an impermeable barrier, vertical or horizontal in nature, as well as fracturing in the host rock.

With regards to the town of Beaufort West, we find numerous hydrogeological reports assessing the well fields, which are located north of the town (Figure 1) for municipal supply. Those reports up until 1980 have been compiled and assessed.[22] Kotze *et al.*[20] have utilised this data and shown short-term water level fluctuations in the municipal well fields, but there is a definite decline in water levels in general.[23]

Vogel *et al.*[8] also proved that localised recharge, which is the addition of water to groundwater, occurs in the immediate vicinity of the town. Rose and Conrad[24]concur with this and prove conclusively, by means of isotopic analysis, that surface water and groundwater supplies are not linked. Furthermore, groundwater to the south of the town is more saline than the groundwater in the well fields to the north.[8] This also suggests that the two groundwater systems are separated by the town dyke.

More recently, Nhleko and Dondo[25] looked at regional flow of groundwater in the vicinity of the town of Beaufort West. Correlations of geological logs, digital elevation models and three-dimensional cross-sections were all utilised in order to understand the hydrogeological setting of these three aquifers. The study highlighted the fact that groundwater resources in the area are slowly depleting and more research is required in order to fully understand the aquifers and thus maximise their use.[25] It was also shown that flow is generally in a southerly direction and that both the town dyke and Hansriver dyke in the area appear to act as flow barriers to groundwater, which compartmentalises the groundwater dynamics into north, middle and south regions. Moreover, the three compartments are linked by the Gamka River and its tributaries which overflow the dykes. Nhleko and Ndondo[25] also suggested that all the data for boreholes should be captured, specifically water strikes, as this plays a major role in determining which aquifers are being intersected as well as their yield.

Results

The results from the radioactivity analysis do not highlight any anomalous points of interest (Table 1). Steenrotsfontein's higher radioactivity values could be attributed to the fact that the sample is located within a region of anomalously higher Uranium. These values should have been expected considering the fact that the majority of the previously mentioned hydrogeochemical data sets allude to this.[16] Furthermore, it has been shown that the uranium deposits are of a "marginal" grade and this must be the reason for the minimal amounts of Uranium being liberated into the groundwater.[15]

The concurrence with previous data sets proves that the methods of sampling and analysis used in the field are acceptable for radioactivity sampling and could be used for further studies.

Table 1. Radioactivity results stemming from the study area (values in $mBq\,L^{-1}$).

	Radioactive elements tested for in sample										
Sample name	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Po	^{235}U	^{227}Th	^{223}Ra	^{232}Th	^{228}Th	^{224}Ra
Steenrotsfontein	641	1380	15.1	12.9	4.86	29.5	6.79	10.9	2.3	13.9	6.94
Town Spring	184	465	7.9	1.6	5.68	8.49	7.3	4.85	2.83	3.9	1.6
Blydskap 1	123	554	7.9	9.49	6.56	5.68	2	–1	1.3	1.8	3.18
Blydskap 2	158	584	6.3	16.4	6.91	7.3	2.4	–1.5	0.81	2.2	1.5
Scheurfontein	135	380	6.8	6.07	0.98	6.51	2.5	0.47	1.27	0.42	0.68

Sampling protocol

The protocol was developed using the inputs from the methods previously outlined. Furthermore, the results from the field sampling exercise played a major role in interpreting and understanding the possible application of the protocol within a South African context. The most important aspects of the protocol are outlined below in order to showcase its efficacy. The entire protocol can be examined in Xu *et al.*[14]

Screening methods used to determine radioactivity in fractured rock aquifers

These methods make use of the detection of Radon gas in order to ascertain whether the groundwater is radioactive. This aids in determining whether a sample should be sent for further laboratory analysis for radionuclides. Thus costs could be minimised and no unnecessary work is done. The screening methods also give the individual an opportunity carry out *in situ* analysis and thus reduce the probability of incorrect sample analysis, due to prolonged storage periods, degassing or transportation. Some of the most commonly used methods are:

- Alpha Card Method
- Alpha scintillation counting
- Electret Ion Chamber (EIC)
- Liquid scintillation counting (LSC)

Zhou *et al.*[26] made use of alpha scintillation counting in conjunction with a Radon bubbler. Thus the gas was stripped from the groundwater sample by the bubbler and an alpha counter was used to determine the Radon concentration. This seems to be an effective combination of two methods.

Lin[27] has utilised the alpha card method in the Table Mountain Group, South Africa. Wu *et al.*[28] extensively explain the field operation procedure of the aforementioned machinery. It works on the principle of stripping the Radon gas from the vadose zone gas, the equipment is also able to bubble the Radon gas out of water. The emanating gas is then measured in a gas proportional counter. Lin[27] states that the count is termed pulse number in the alpha card instrument, from which the concentration of the radon gas can be estimated by means of the following equation:

$$C_{Rn} = JN_{RaA}$$

where C_{Rn} is the concentration of Radon, N_{RaA} is the pulse number measures and J is the coefficient of the Radon concentration which is a constant and is fixed by the measuring equipment.

Amrani *et al.*[29] have compared the LSC and EIC methods. The former method measures the Radon concentration in units per time. Thus a conversion is required in order to acquire the reading in $Bq\,L^{-1}$. The latter measures voltage and then the original Radon concentration in the water is inferred. The LSC method allows the equilibration of the Radon gas into an organic "cocktail", whilst the EIC allows the Radon to enter a chamber by passive diffusion.

Pre-sampling procedures

Weaver *et al.*[13] outlines a comprehensive planning programme which delves into pre-sampling procedures. This includes a list of field equipment and general groundwater sampling procedures. These practical tips are of the utmost importance when preparing to venture into the field.

Another important aspect is acquiring permission from land owners. In many instances, boreholes are located on private property and it is crucial that farmers or landowners are consulted prior to sampling. This process is also helpful in the hydrocensus, which is the initial phase of data collection, due to the fact that the land owner could provide valuable information with regards to numerous environmental factors in the area as well as history, and the location of wells and springs.

Last, it is necessary to liaise with the laboratory in order to ascertain which containers, preservatives and reagents are to be used when sampling for radionuclides.[13] Wilde *et al.*[30] suggest that a 1-L polyethelyne bottle be acid rinsed and then the sample should be preserved to $pH < 2$ using HNO_3. Levin,[31] on the other hand, states that sample bottles should be thoroughly rinsed with 10% HCl and then emptied and rinsed thrice with de-ionised water.

Previously used bottles should be rinsed with acid and soaked in de-ionised water for a few days before sampling.[13] New sample bottles, on the other hand, should be field rinsed with water directly from the sampling device.[30] Finally, the sample bottle should preferably be plastic, due to the fact that glass could break and thus leakage would occur and therefore sample integrity would be questionable.[31]

Downhole logging

Prior to purging it is suggested that downhole logging is done. This will help to identify fractures within the sub-surface.[3] Anomalous increases in certain parameters infer the location of a fracture within the borehole. This would only occur if the well is screened at various intervals, or is entirely uncased. Furthermore, various *in situ* parameters such as temperature, pH, electrical conductivity, dissolved oxygen as well as some dissolved ion concentration could be determined in the borehole, depending on the type of logging tool used.[13]

Purging

Before taking a sample, the well should be purged. This is done in order to remove the stagnant water. Cook[3] has compared sampling prior to purging as well as post purging. The author has concluded that the Radon concentration within the well varies greatly due to the ability of the gas to diffuse. Thus a sample taken from an unpurged well would not be representative of *in situ* conditions of the aquifer. This is especially true in fractured rock aquifers due to preferential pathways (Figure 2).

Also the well should be purged using a low flow approach.[32] This minimises the oxidation of the sample and thus the alteration of *in situ* chemical conditions. After the borehole has been purged the fractures would then be de-watered, followed by the matrix.[3] This has important implications for chemical analysis as the conditions within a fracture differ to those of the matrix. It is especially important with regards to radionuclides due to the fact that we find an increase in Radon within these fractures.[33] Cook[3] has shown that the volume of water which should be purged must equate to two well volumes. It is critical to note that low flow sampling does not equate to purging.[13]

After purging the well, the use of a flow-through cell would be advised. This is done in order not to expose the sample to the atmosphere and thus alter its chemical or physical state.[13] The flow-through cell seems to be the best tool for direct field measurements, due to the ability of the device to measure multiple parameters.[30] When taking the sample the utmost care should be taken in order not to contaminate the sample.

Some parameters are measured in the field for the following reasons:[13]

- to check the efficiency of purging
- to obtain reliable values of those measurements that will change in the bottles during transport to the laboratory
- to obtain some values that may be needed to decide on the procedure or sampling sequence immediately during the sampling run

The parameters which are normally taken *in situ* include pH, Eh, temperature and electrical conductivity.

Sampling devices

It is also of the utmost importance that the acquired sample is representative of the *in situ* conditions.[30] Thus the devices used in order to sample the groundwater are very important.

Puls and Barcelona[32] strongly recommend that low flow sampling, in conjunction with packers, should be carried out in fractured rock aquifers. This approach should only be attempted after identifying the water bearing fractures and thus the sampling zone can be isolated.

Depth specific samplers have also been proposed as a viable option.[13] These are lowered into the borehole in order to gain a sample at the fracture or other area of interest. Unfortunately, this method could artificially elevate turbidity in the well due to it disturbing the water while it is submerged.[34]

A relatively new method for sampling is known as Diffusive Gradient in Thin Films (DGT). These are based on the use of a

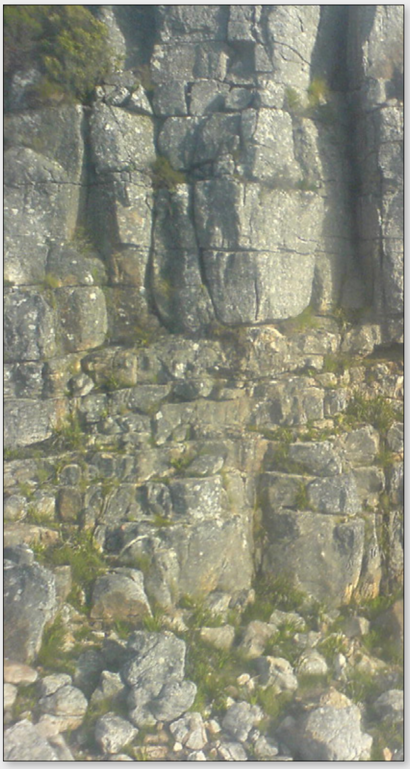

Figure 2. Vertical and horizontal fractures in sedimentary rocks act as preferential pathways for groundwater recharge and flow.

chelator, which is an iron binding complex, in order to sample metals over a time period of a few days. Numerous case studies have been outlined and these show the applicability as well as the functioning of this specific method.[35] Furthermore, a phosphate-based DGT has been developed specifically for radioactive elements.

Sampling frequency

EPA[36] promotes the hourly sampling of fractured aquifers for field determinands. This protocol was developed specifically for nuclear waste facilities and the parameters which would be measured on an hourly basis would include those which a data logger could determine. These include temperature, TDS and water level. This would aid in determining whether leakage has occurred from the storage facility and also aid in determining anomalous inflows of contaminants in groundwater, in a natural setting. The aforementioned could be inferred from fluctuations in readings and the parameters would act as indicators for the contamination of groundwater.

A statistical analysis could also be done in order to effectively ascertain sampling frequency. This would mean that a substantial amount of data would be required and it would have to stem from the area of interest. As a crude guideline you need about five samples from groundwater source with seasonal variation to indicate variability.[37]

The purpose of trend analysis, in statistical terms, is a determination of whether the probability distribution from a series of observations has changed over time.[38] The simplest statistical method which could be used to ascertain this variability would have to be based on historical data, as previously mentioned.[39]

The theory of sampling applied

Petersen *et al.*[40] has extensively examined the Theory of Sampling (TOS) in relation to data analysis and unbiased results. Helsel and Hirsch[38] have highlighted the use of statistical methods in order to examine data, graphically represent data and include aspects of quality control of data for error mitigation in interpretation. The latter text was included in the protocol whereas the former was unfortunately not.

The TOS, as a science, could add an extensive value to this protocol. It is felt that the major point being driven home by Petersen *et al.*[40] is the fact that the quality control of a sample is the responsibility of everyone within the entire analytical chain. This point is taken quite lightly in sampling for groundwater due to the fact that certain laboratories are negligent of cross-contamination and sample storage. This in turn has an adverse effect on sample integrity and in turn the results. This is known as the Increment Preparation (IPE) error in TOS and includes every step after extraction.

The Fundamental Sampling Error (FSE) as well as Grouping and Segregation Error (GSE) are common, especially in the hydrological sciences. It has been shown that *in situ* practices, especially in surface water, still advocate grab samples which are in no way representative of the lot.[41]

Conclusions

A groundwater sampling protocol for radioactive elements in fractured rocks, which was developed using international best practices as well as local methodologies, proves that previously utilised methods are extremely effective. This protocol covers a wide range of methods for pre-sampling, sampling and post-sampling processes. Historical data in conjunction with the newly generated data set, stemming from this study, conclusively prove that the methods outlined by Weaver *at al.*[13] for sampling radioactive elements are applicable to fractured rocks.

Unfortunately, due to limited infrastructure as well as field conditions, not all the methods outlined in the protocol could be tested. Therefore, it is suggested that the other methods outlined in the document should be applied in the field and the efficacy thereof should be scrutinised in future studies. A methodology for this could be utlilising multiple methods, like low flow sampling as well depth specific sampling on a single well and then comparing the results in order to check whether the radioactivity results are similar.[32,8]

TOS should also be applied to the development of future manuals in order to align sampling in the hydrological sciences with sampling as a science. Petersen *et al.*[40] have shown that sampling as a science is still developing due to the fact that it is merely 50-years old. In order to better the science geostatistical applications such as variographic analysis of time series type data, which is a practical tool for optimising the sampling frequency of heterogeneous sampling targets and could be applied in future studies.[4]

The exercise was also hindered by the fact that many mines have bought prospecting rights from farmers in the area. Thus farms which are currently being explored for uranium could not be accessed for research purposes. Despite this, a framework for a sampling protocol was developed in order to aid in better sampling practices.

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