Potential Use of Emerging Organic Contaminants as Pollution Source Tracers

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Abstract

This study investigated the use of emerging organic contaminants (EOCs) as potential pollution source tracers. Water samples were collected from the Blesbokspruit, boreholes and nearby old mine voids and analysed them for EOCs. Caffeine and atrazine were detected at all sampling sites, whilst estrone and terbuthylazine were not detected in any of the mine voids. Although estrone appeared with the lowest frequency, it displayed high concentrations at sites where it was detected. The findings showed the suitability of using EOCs as potential tracers, even at low concentrations.

Keywords: Emerging contaminants, Groundwater, Mine voids, Tracers

Introduction

Emerging organic contaminants (EOCs) are a threat to the aquatic environment due to their persistent nature and their ability to cause health effects to humans and other living organisms, even at low concentrations. EOCs can find their way into the subsurface environment in various ways, including runoff and infiltration from old or recent leaking infrastructure and inadequate removal during water treatment (McCance *et al*. 2020).

Many emerging contaminants are being assessed for their suitability as contamination source tracers. McCance *et al*. (2018) summarised the criteria that should be followed when selecting ideal groundwater tracers: they should be released in sufficient quantities from the pollution source, persistent in the aquatic environment, and responsive to sensitive analyses. Several scholars have tested the use of compounds such as carbamazepine, estrone, caffeine, acesulfame, bisphenol-A, simazine, atrazine and many others as tracers. Some of these can directly be linked to their specific source and/or use (James *et al*. 2016), whereas some may emerge from more than one pollution source. McCance *et al*. (2020) stressed a need for EOC assessment in environments represented by different hydrogeological settings and contamination sources so that the methods can also be used in other settings.

This study assessed the potential usage of six EOCs as pollution tracers in the Witwatersrand Goldfields. These compounds are thought to emerge from anthropogenic activities and were frequently detected at the study sites.

Site Setting

Study area

The current study focussed on the Blesbokspruit, which is a stream that passes through the Eastern Basin of the Witwatersrand (fig. 1). Studies that have been conducted by the Council for Geoscience (CGS) in these areas have shown that little, if any, surface water flows into the underground workings near the large north-south channel of the Blesbokspruit. Therefore, much of the surface water that enters comes from areas upstream of the Geduld, Alexander, and Cowles Dams that act as a tributary to the Blesbokspruit. Thus, the Blesbokspruit receives mixing of water from various sources, including pollution sources such as runoff, sewage and industrial discharges.

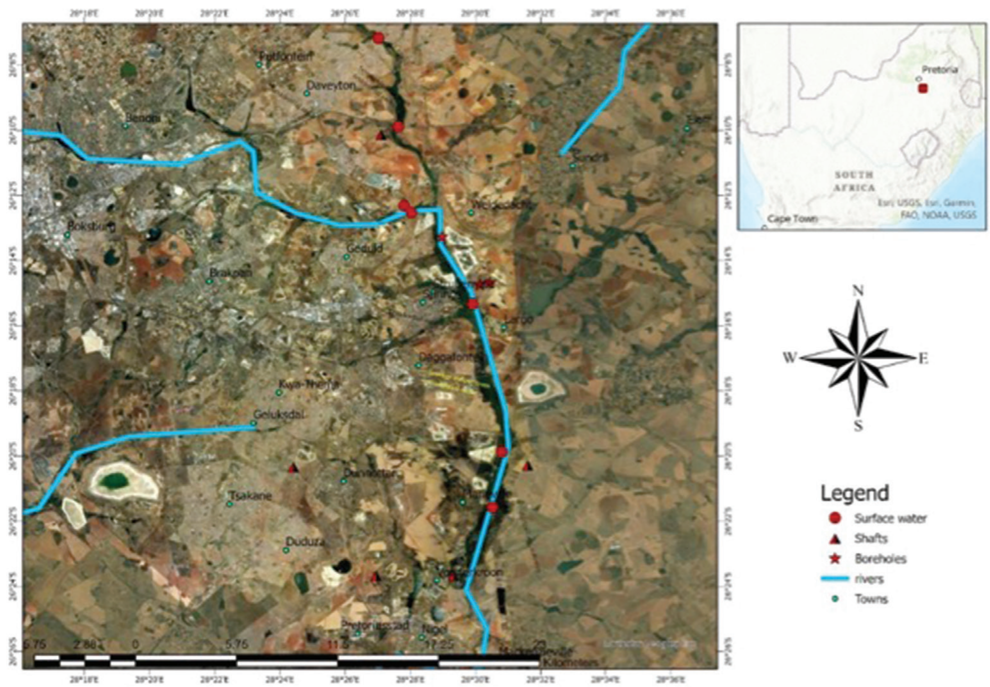

Figure 1 *Study area*

Ethical considerations

The current study relied on emerging contaminants that had been released into the environment through anthropogenic activities. Therefore, no compounds were injected into the environment.

Sampling and analytical procedures

Water samples were collected from the Blesbokspruit, old mine shafts and surrounding boreholes (fig. 1) for the analyses of EOCs. Plastic bailers were used to collect water from both boreholes and mine voids from below the static water level. A bucket was used to grab samples from the surface water bodies. Non-preserved 250 ml glass bottles were used to store the water samples, and, prior to filling, these were rinsed with the sample water. The samples were then stored inside a cooler box and kept for a maximum of 7 days under these dark and cold conditions.

The samples were transported to the Microbial Biochemical and Food Biotechnology Laboratory, University of the Free State where they were analysed for EOCs. Samples were processed with solid phase extraction using Waters Oasis HLB cartridges.

Data interpretation

Data from the laboratory was interpreted using the Statistical Package for Social Sciences (SPSS). Spearman Rank Correlations were done to test the correlation between the variables, whereas descriptive statistics (frequencies) were calculated to determine the detection frequency of each compound per site. Microsoft Excel was used to create bar graphs for the EOC concentrations.

Activities around the area

There are several activities on-going around the study area that may result in the discharge of anthropogenic pollutants into the aquatic environment, i.e. agriculture, sewage discharges from residential areas, landfill drainage, run-off, mining and mine tailings (fig. 1). Considering all the potential pollution sources in the area, analyses looked at compounds that might emerge from such sources. The compounds that were considered for interpretations

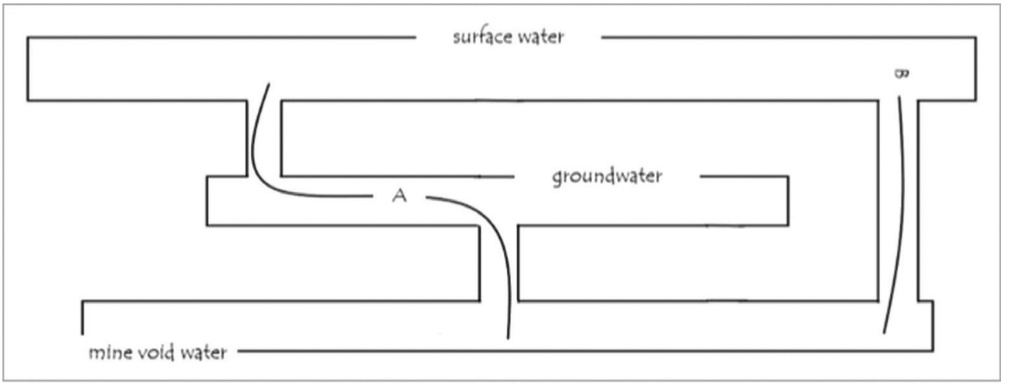

Figure 2 *Possible contaminant pathways into the mine voids.*

are: the life-style compound caffeine, the herbicides atrazine and terbuthylazine, the pharmaceutical carbamazepine, a hormone (estrone), and the industrial compound bisphenol-A. These six were chosen because their frequent occurrence in the aquatic system showed their potential to be used as tracers and/or co-tracers.

Contaminants pathway

The contaminants are assumed to enter the subsurface through different routes (fig. 2). These can be a direct pathway, from the surface to the mine voids (route B) and/or indirectly, where surface water recharges groundwater, and then flows through the mine voids (route A).

Results and Discussions

Caffeine

Caffeine is a psychoactive drug. This compound is normally detected frequently in the aquatic environment because of its widespread consumption (Sui *et al.* 2015). Due to this characteristic, caffeine was detected in all the current study samples, though the concentrations varied immensely. The highest concentration detected was 15.70 ng/mL in a surface water sample, whilst the lowest concentration was 0.01 ng/mL in a groundwater sample. The sample that measured the highest concentration of this compound was collected in an area that receives a mixture of clean water with sewage discharges from residential areas.

Herbicides

Atrazine and terbuthylazine are widely used herbicides. Atrazine is known to be persistent for long periods in groundwater (Lapworth *et al.* 2015). It was detected at all the sampling sites, with the highest concentration of 1.20 ng/mL measured in the surface water sample. Although atrazine was detected in all the samples, most of the concentrations were <0.05 ng/mL.

Terbuthylazine was detected in all the surface water and groundwater samples, and was not detected in the mine voids samples. The concentrations measured ranged between 0.003 and 0.37 ng/mL for groundwater and surface water samples, respectively. The concentrations measured for the surface water samples were greater than in the groundwater samples. There is enormous agricultural work going on in the study area, although no major concentrations of herbicides were measured.

Bisphenol-A

Bisphenol-A is an industrial compound that is used to make plastics and resins. This compound is described as less persistent under aerobic conditions and more persistent in anaerobic conditions (Lapworth *et al.* 2015). It was detected in all the mine void and groundwater samples, except for one borehole (BH10). This compound was also detected in 1 out of 7 surface water samples. The highest concentration measured for this compound was 2.15 ng/mL in a mine void sample, with the lowest concentration of 0.29 ng/mL measured in a groundwater sample.

Carbamazepine

Carbamazepine is a pharmaceutical drug used for the treatment of epilepsy and neuropathy. This compound can survive and remain unchanged after years of travel in the subsurface, with minor degradation and adsorption (Sui *et al.* 2015). In the current study, carbamazepine was detected at concentrations between 0.04 and 0.70 ng/mL. The highest concentrations were measured in the surface water samples, with no concentration detected in the groundwater samples.

Estrone

Estrone is a steroid hormone that has been described as a compound with high potential to degrade in stream sediments under aerobic conditions (Bradley *et al.* 2009). Estrone was not detected in most of the sites, although where detected, it occurred in high concentrations. The highest concentrations for estrone were 14.10 ng/mL and 13.40 ng/mL in surface water and groundwater samples, respectively. This compound was not detected in the mine void samples.

Detection frequency

Detection frequency was tested for all the compounds at each site and these are presented as percentages (Table 1) and bar graphs (fig. 3). Table 1 shows that caffeine and atrazine were detected at 100% of the sampled sites, possibly due to their wide usage in the area and persistent behaviour, respectively. These two were followed by terbuthylazine at 68.8%. Although estrone displayed high concentrations at sites where it was detected, this compound was the least frequently detected. It was detected at 5 of the 16 sampling sites. Carbamazepine appears to be normally distributed at the sites where it was detected (fig. 3).

Relationship Between Specific Sites

Surface water and groundwater

To assess the potential use of EOCs as tracers of pollution, Spearman Rank Correlations between sites were determined. Table 2

***Table 1** Detection frequency of compounds in 16 sites of interest.*

Compounds	Caffeine	Atrazine	Bisphenol-A	Carbamazepine	Estrone	Terbuthylazine
Sites	16	16	16	16	16	16
Frequency	16	16	9	9	5	11
Percentage (%)	100.0	100.0	56.3	56.3	31.3	68.8

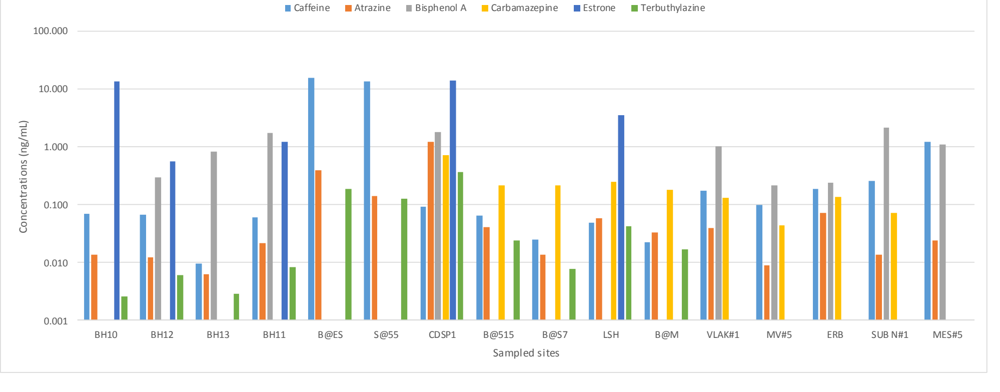

***Figure 3** EOCs concentrations per site (Boreholes (BH), Blesbokspruit at Eiselen Street (B@ES), Sewage inflow to Blesbokspruit (S@55), Cowles Dam outflow (CDSP1), Blesbokspruit downstream (B@515), Blesbokspruit upstream (B@S7), Largo Sinkholes (LSH), Blesbokspruit at Marievale (B@M), Vlakfontein Shaft 1 (VLAK#1), Marievale Shaft 5 (MV#5), Eastern Basin Treatment Plant (ERB), Sub Nigel Shaft 1 (SUBN#1), Modder East Shaft 5 (MES#5).*

Table 2 Spearman Rank Correlation between borehole and surface water samples.

	BH 10	BH 12	BH 13	BH 11	B@ES	S@55	CDSP - 1	B@515	B@S7	LSH
BH 12	.551									
BH 13	-.191	.290								
BH 11	.290	.943	.551							
B@ES	.400	-.152	.400	-.152						
S@55	.400	-.152	.400	-.152	1.000					
CDSP - 1	.087	.600	-.174	.543	-.698	-.698				
B@515	-.191	-.754	-.191	-.754	.400	.400	-.696			
B@S7	-.191	-.754	-.191	-.754	.400	.400	-.696	1.000		
LSH	.493	.029	-.812	-.257	-.213	-.213	.314	.232	.232	
B@M	-.250	-.812	-.250	-.812*	.339	.339	-.522	.941	.941	.290

displays the relationships between surface water and groundwater. Most of the surface water samples displayed moderate to strong correlation with groundwater samples. The samples that did not show any relationship were collected from Blesbokspruit at Eiselen Street (B@ES), which is upstream of the study area.

Surface water and mine voids

Since it is stated that other possible pathways of contaminants to the subsurface may include surface water directly entering the mine voids, interpretations also looked at this aspect. Strong positive correlations were only observed for surface water or mine voids samples amongst each other (table 3). Lack of relationship between surface water and mine voids could possibly be resulting from the following: (a) mine voids receiving EOCs contributions from other sources of pollution other than the Blesbokspruit, (b) no direct contribution from surface water into the mine voids in this area (no water ingress).

Groundwater and mine voids

Table 4 displays the relationship between groundwater and mine voids samples. Most of the groundwater showed a weak correlation with the mine voids. The only strong relationship in this regard was between one groundwater and a mine void sample. This mine void sample is located upstream of the Blesbokspruit, whilst the borehole is situated mid-stream. Although all the boreholes are situated mid-stream near most of the shafts (mine voids), a strong relationship could not be observed between these, further confirming that there is no water ingress from this source.

Conclusions

This study investigated the potential use of six organic compounds as pollution tracers. The detection of compounds in groundwater and mine voids is a good indication that these can potentially be used as pollution tracers.

Although most compounds were detected in the subsurface, it was concluded that surface

Table 3 Spearman Rank ***Correlation between surface water and mine voids samples.***

	B@ES	S@55	CDSP - 1	B@515	B@S7	LSH	B@M	Vlak#1	MV#5	ERB	SUB N#1
S@55	1.000										
CDSP - 1	-.698	-.698									
B@515	.400	.400	-.696								
B@S7	.400	.400	-.696	1.000							
LSH	-.213	-.213	.314	.232	.232						
B@M	.339	.339	-.522	.941	.941	.290					
Vlak#1	.031	.031	-.145	.191	.191	-.493	.074				
MV#5	.031	.031	-.145	.191	.191	-.493	.074	1.000			
ERB	.031	.031	-.145	.191	.191	-.493	.074	1.000	1.000		
SUB N#1	.031	.031	-.145	.191	.191	-.493	.074	1.000	1.000	1.000	
MES#5	.548	.548	-.273	.062	.062	-.516	-.062	.770	.770	.770	.770

Table 4 Spearman Rank ***Correlation between borehole and mine voids samples.***

	BH 10	BH 12	BH 13	BH 11	Vlak#1	MV#5	ERB	SUB N#1
BH 12	.551							
BH 13	-.191	.290						
BH 11	.290	.943	.551					
Vlak#1	-.471	.087	.721	.348				
MV#5	-.471	.087	.721	.348	1.000			
ERB	-.471	.087	.721	.348	1.000	1.000		
SUB N#1	-.471	.087	.721	.348	1.000	1.000	1.000	
MES#5	.062	.334	.893	.516	.770	.770	.770	.770

water was flowing into the groundwater and mine voids. The exact source of the tracers could not be apportioned to the surface water samples collected. This could be due to mixing of these water sources with various unsampled sources.

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