Application of Anthropogenic Organic Contaminants for the Determination of Water Ingress in the Witwatersrand Goldfields Mine Voids

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Abstract

Historical mining has led to environmental degradation in the Witwatersrand Goldfields ever since mining companies ceased pumping water from the mines. A study of using emerging organic contaminants as tracers to map the sources and pathways of water ingress into the mine voids is underway. Water samples from the surface, boreholes and shafts were collected and analysed. Atrazine and caffeine were the most persistent and displayed average concentrations of 0.176 ng/mL and 0.793 ng/mL in surface water respectively. Bisphenol A showed high concentrations in the subsurface with averages of 0.162 ng/mL and 1.082 ng/mL for wet and dry seasons respectively.

Keywords: Mine Voids, Organic Contaminants, Surface Water, Tracers

Introduction

Contaminants such as manure and biosolid derived reach the groundwater system through surface water-groundwater exchange from run-off (Focazio *et al* 2008). Nevertheless, these pollutants are not contained in high concentrations that are toxic because of natural attenuation and/or dilution (Lapworth *et al* 2012). In cases where contaminants are found in high concentration levels in surface waters, it shows that there could be a direct input from wastewater sources, or the process of attenuation or dilution is less in surface water as compared to groundwater. However, it was further described that karstic and shallow alluvial aquifers are the most vulnerable to contamination due to limited attenuation because of rapid flow during recharge of those aquifers. Thus, the residence time in these systems is short.

The study conducted by Lapworth *et al* (2012) on injecting emerging organic contaminants (EOCs) as tracers in the subsurface showed that as much as natural attenuation is high for most compounds, it is not complete since some compounds still behave in a conservative way during the process. Several researchers have recently written about the use of emerging contaminants as tracers in surface water, groundwater and drinking water. These emerging contaminants comprise compounds such as caffeine, nicotine derivatives, carbamazepine, clofibric acid, benzotriazole, bisphenol, gemfibrozil (Murray, Thomas and Bodour 2010); (Lapworth *et al* 2012). Concentrations of emerging contaminants (pesticides, industrial, pharmaceuticals and personal care products) may be traced in drinking water, surface water, groundwater or in the environmental discharges such as waste water from treatment plants (Murray, Thomas and Bodour 2010).

This study evaluated the application of EOCs to trace water ingress in the Witwatersrand Goldfields. It further utilised eleven compounds commonly found in wastewater discharges. Pearson correlation and Dendrogram analysis were used as complementary methods to display correlation and cluster sites with similarities in terms of organic contaminants found, respectively.

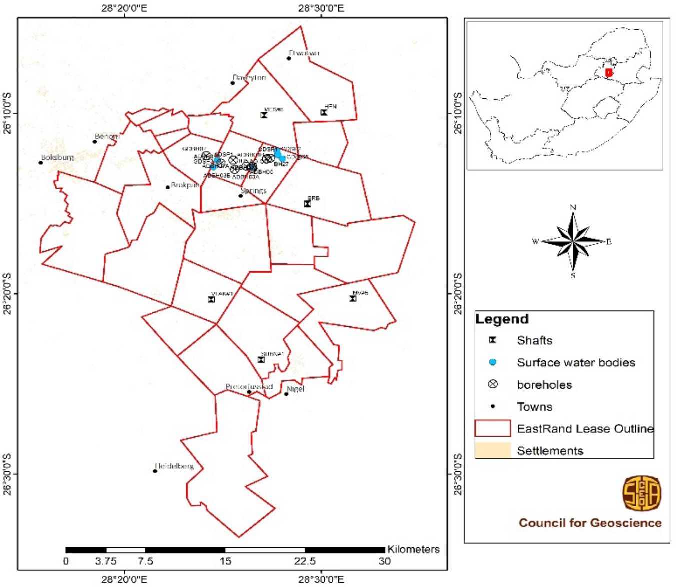

Figure 1 *Locality map of the Eastern Basin.*

Methods

Study area

The study was conducted in the Eastern Basin of the Witwatersrand Goldfields (fig. 1). Surface water bodies, boreholes and shafts were sampled.

Ethical considerations

There were no compounds injected into the environment during this study. Thus, the study is analysing EOCs that are introduced into the aquatic system from point and diffuse sources of contamination. These are compounds used and released into the environment on a daily basis.

Sampling and analytical procedure

Water samples were collected during the wet and dry seasons from shafts, surface water and boreholes for the analyses of EOCs. Seasonal sampling was done to identify seasonal changes in the compounds concentration in the water. Prior collecting groundwater samples, boreholes were purged to remove bore well storage. Plastic bailers were used to acquire samples from boreholes and shafts at the static water level. Water samples from the surface water bodies were collected using the sampling bottles or buckets in areas where water could not be reached easily. A 250 ml glass bottle that was rinsed with water to be sampled was filled at each sampling site for the storage of water for organic contaminants analyses. Samples were stored under cold conditions immediately after sampling and kept for a maximum of 7 days before transported to the laboratory for analyses.

The water was analysed at the Microbial Biochemical and Food Biotechnology Laboratory, University of the Free State.

Samples were processed using solid-phase extraction using Waters Oasis HLB cartridges. Two separate analyses were performed on the eluates:

- Analysis of underivatised samples using targeted MRMs; and
- Analysis of eluates after derivatisation using dansyl chloride. Six labelled internal standards were used to compensate for matrix effects and instrument drift.

Data interpretation

Laboratory data was exported to the Statistical Package for Social Sciences (SPSS) for further statistical evaluation. Statistics tools such as Hierarchical cluster analysis (HCA) and Pearson correlation plots were done. Furthermore, Microsoft Excel was used to draw graphs that were used for further interpretations.

Results and discussion

Tracers that were analysed in the surface, groundwater and mine voids water for both seasons were metolachlor, caffeine, atrazine, bisphenol A, carbamazepine, diclofenac, estradiol, estrone, ibuprofen, sulfamethoxazole and terbuthylazine. Some of the compounds were either not traced from the water completely, or were below limit of quantification (LOQ).

Occurrence of EOCs in aquatic environments and mine voids

Twenty-two surface water bodies, 28 boreholes and 1 shaft were sampled during the wet season of this study. During the dry season, the same sites were sampled, with five more shafts added to the sampling run making 6 shafts.

Tab.1 displays the average calculated for each compound for the results obtained for the wet and dry seasons in surface water, groundwater and water from the mine voids.

Compounds such as diclofenac, estradiol, estrone and terbuthylazine were either below LOQ or not traced in the mine voids water. Ten orders of magnitude high concentrations were observed for the dry season as opposed to the wet season that displayed low concentrations. This can be explained by the concept of dilution that is assumed to have taken place during the wet season when recharge occurred.

EOCs concentrations in surface water, groundwater and mine voids water

Fig. 2 indicates concentrations variation from surface water bodies to groundwater and then mine voids. Shafts are presented by sites VLAK#1 to ERB, surface bodies by GDSP3 to CDSP2 and boreholes by GDBH02 to BH33. Atrazine and caffeine appear to be found in almost all sites. This could be explained by the persistent behaviour (Schwab, Splichal and Banks 2006) and high usage (Sui *et al* 2015) of these compounds respectively. Bisphenol A also appears to be occurring in all sites, but with high concentrations displayed in water samples collected from boreholes and shafts as opposed to those taken from the surface water bodies. Lapworth *et al* 2015 explained that bisphenol A is more persistent under anaerobic conditions, which explains this observation. Terbuthylazine was traced in all surface water bodies and almost all boreholes, but not in any of the mine voids. Carbamazepine was also traced in all surface water, some boreholes and mine voids. Metolachlor was detected in almost all sites except few boreholes, whilst sulfamethoxazole was mostly traced in surface water and some shafts, but not in groundwater.

Table 1 *EOCs average seasonal variations.*

		Average (Wet season)			Average (Dry season)			
Compounds (ng/mL)	**Purpose**	**SW**	**GW**	**MV**	**SW**	**GW**	**MV**	**LOQ**
Atrazine	Herbicide	0.097	0.024	0.023	0.255	0.036	0.026	0.001
Bisphenol A	Industrial compound	0.052	0.162	0.055	0.272	1.082	1.041	0.01
Caffeine	Psychoactive drug	0.096	0.030	0.036	1.489	0.091	0.329	0.001
Carbamazepine	Pharmaceutical	0.117	0.027	0.019	0.469	0.060	0.064	0.01
Diclofenac	Pharmaceutical	0.017	0.002	0.001	0.059	0.001	0.001	0.001
Estradiol	Sex hormone	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Estrone	Sex hormone	0.1	0.1	0. 1	1.459	1.896	0.1	0.1
Ibuprofen	Pharmaceutical	0.148	0.002	0.001	0.327	0.001	0.013	0.001
Metolachlor	Herbicide	0.034	0.001	0.001	0.053	0.003	0.040	0.001
Sulfamethoxazole	Pharmaceutical	0.036	0.01	0.01	0.470	0.019	0.012	0.01
Terbuthylazine	Herbicide	0.087	0.005	0.002	0.122	0.008	0.001	0.001

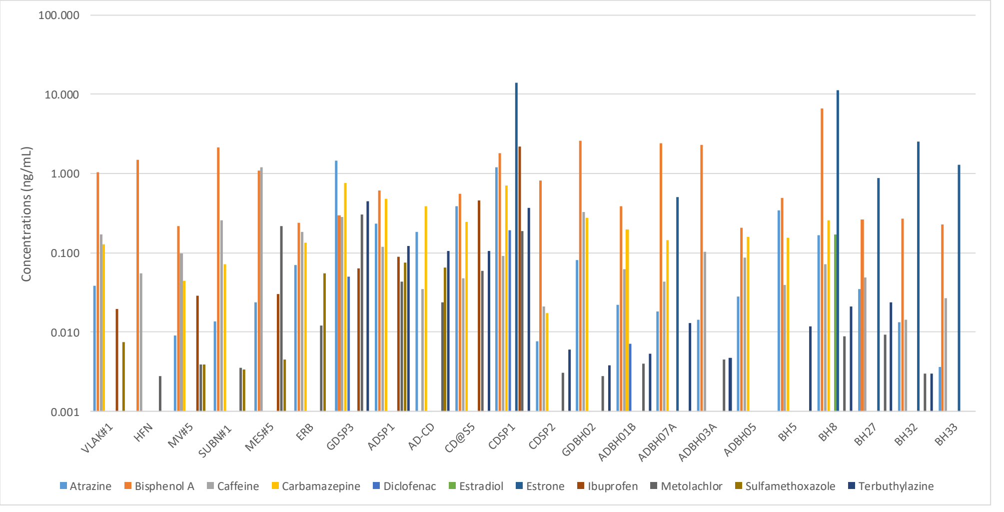

Figure 2 *EOCs concentration variations from surface bodies, boreholes and shafts.*

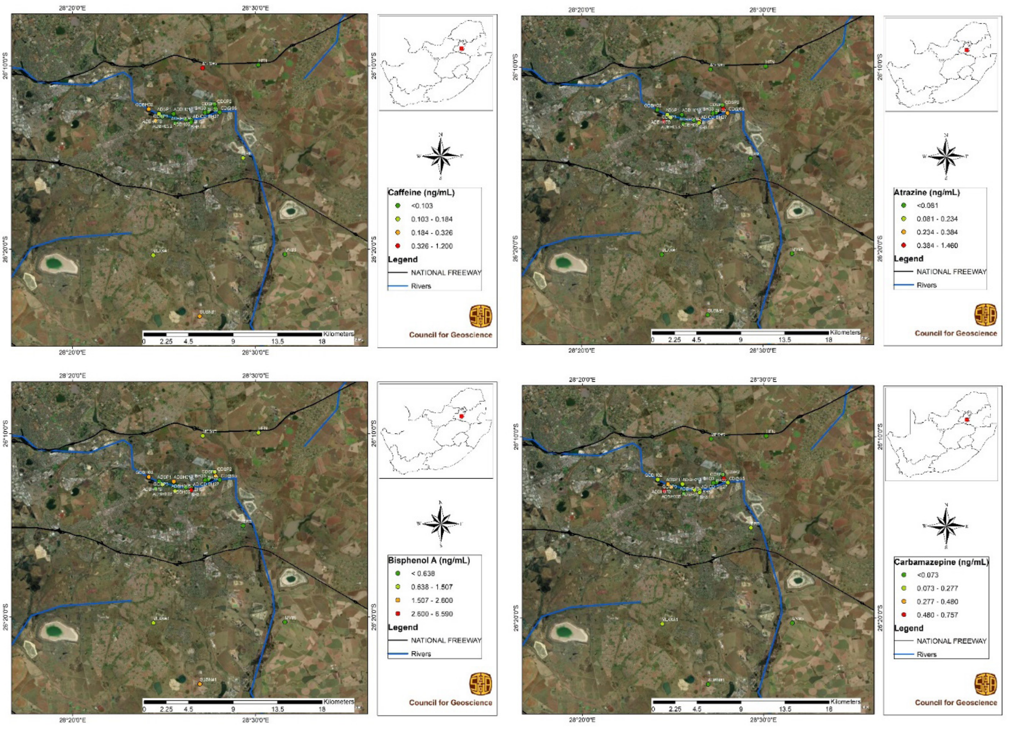

Figure 3 *Compound concentration maps for caffeine, atrazine, bisphenol A and carbamazepine.*

EOCs concentration maps

Compounds maps for caffeine, carbamazepine, bisphenol A and atrazine (fig. 3) were done to display the changes of concentrations from surface water to groundwater and mine voids water. The findings indicated the exchange between these waters. Atrazine although traced in all (except HFN) sites because of its persistent capabilities, appeared to be slightly high in surface water as compared to subsurface water. Caffeine did not display any particular pattern of occurrence. It had concentrations of >0.103 ng/mL in surface water and shafts. Carbamazepine, unlike others was not traced in some boreholes, especially ones surrounding CD and in shafts HFN and MES#5 that are situated upstream. Lastly, Bisphenol A displayed high concentrations in subsurface sites than what was observed in the surface water.

Statistical analysis

Hierarchical cluster analysis

The dendrogram was produced using the Ward linkage method where five groups were obtained (fig. 4). Group 1 consists of 2 shafts and groundwater from AD. The second group is represented by shaft SUBN#1 and some boreholes surrounding AD. Group 3 clusters CD boreholes together, but with no surface water. Group 4 is the largest and comprises 3 shafts, 4 boreholes and 4 surface bodies.

The findings from these analysis shows surface water, groundwater and mine voids water interaction. Thus, mine voids are receiving water from both surface and groundwater in the surrounding areas.

Bivariate correlation analysis

Pearson correlation results (Tab. 3) indicated interaction relationship between surface and subsurface water. These were observed from high correlation values between the variables. High positive correlation existed amongst the shafts, except for shaft HFN against MES#5 and ERB that displayed a moderate correlation.

High correlations between Alexander Dam (AD) (ADSP1) and the shafts (except MES#5) were observed. Additionally, high relationships were seen between this site and the surrounding groundwater such as ADBH01B, ADBH07A, ADBH05, indicating an interaction between the water.

Further observations were made for sites surrounding the Cowles Dam (CD). Surface water (AD-CD and CDSP1) that were collected at the entrance and exit points of CD displayed low correlations with all sites, except that CDSP1 had a high correlation with the surrounding groundwater. An interaction between surface and groundwater can be deduced from these findings, although it could be "gaining stream" situation.

CDSP2 displayed a high correlation with almost all sites except shafts MES#5 and ERB that were moderate, and the boreholes surrounding CD. The findings therefore gives an indication of surface water interacting with groundwater and mine voids water.

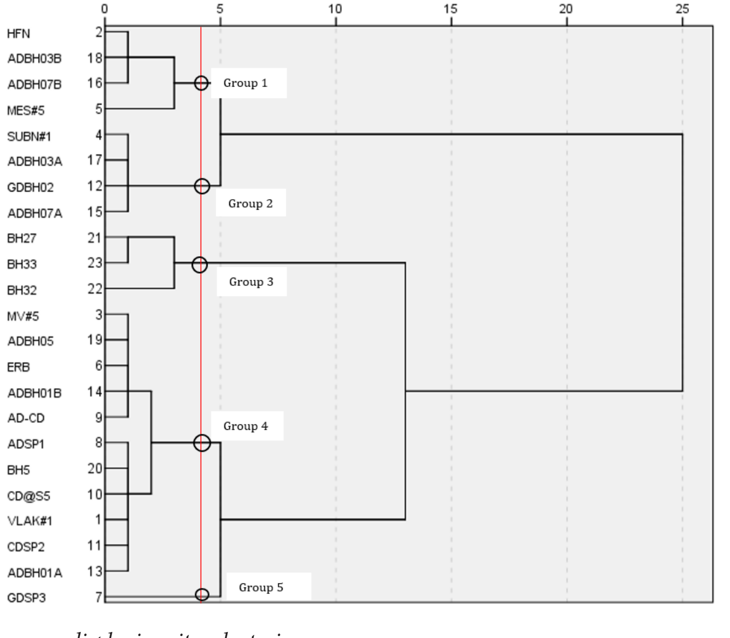

Figure 4 *Dendrogram displaying sites clustering.*

Table 2 *Correlation results as obtained from Pearson correlations.*

	MV#5	SUBN#1	MES#5	ADSP1	CDSP1	CDSP2	ADBH07A	ADBH05	BH8	BH33
MV#5	1									
SUBN#1	**0.939**	1								
MES#5	**0.862**	**0.713**	1							
ADSP1	**0.772**	**0.748**	.448	1						
CDSP1	-.095	-.030	-.141	-.164	1					
CDSP2	**0.905**	**0.995**	0.645	**0.746**	-.016	1				
ADBH07A	**0.869**	**0.97**	.599	**0.713**	.189	**0.978**	1			
ADBH05	**0.864**	**0.773**	0.648	**0.934**	-.126	**0.744**	**0.724**	1		
BH8	.304	.413	.174	.156	**0.887**	.425	0.603	.214	1	
BH33	-.018	.058	-.045	-.134	**0.983**	.068	.272	-.063	**0.931**	1

Conclusions

The application of emerging organic contaminants as tracers in the current study gave an indication of surface-subsurface water interaction. Seasonal sampling results displayed high compound concentrations during the dry season as compared to the wet season. Depending on their behaviour under various conditions, EOCs varied in concentration from surface water, groundwater and mine voids water. Atrazine and caffeine were the most persistent as they were traced in all sites. Bisphenol A was more persistent under anaerobic conditions leading to its high concentration values in subsurface water. The Dendrogram and Pearson correlation results displayed Alexander Dam surrounding sites showing an indication of surface water interacting with subsurface water, whilst, for Cowles Dam, surface water bodies except CDSP1 that had low correlation with shafts did not give an indication of correlation with the surrounding boreholes.

Based on the study findings, it is recommended that a study on understanding precise sources of contamination by EOCs should be considered since this can be utilised in directly identifying some sources of ingress. Additionally, more EOCs that are site specific should be added to the study.

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