

# A cheap and simple passive sampler using silicone rubber for the analysis of surface water by gas chromatography–time of flight mass spectrometry

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## ABSTRACT

Water pollution events may arise rapidly, requiring a methodology that is easy to implement, fast to deploy, and sufficiently sensitive to detect the trace presence of hazardous contaminants. A cheap and easy to use silicone rubber (polydimethylsiloxane (PDMS)) miniature passive sampler is described. In order to test the methodology, pollutants were concentrated, in situ, from surface water in and around Pretoria, South Africa. The versatile sampler allowed for conventional and enhanced sensitivity, solvent-free analysis by comprehensive gas chromatography – time of flight mass spectrometry (GCxGC-TOFMS) and high resolution TOFMS (GC-HRT). Contaminants detected in surface water include caffeine, personal care products, pharmaceuticals, pesticides and polycyclic aromatic hydrocarbons.

**Keywords:** passive sampler, silicone rubber (PDMS) tubing, GCxGC-TOFMS, GC-HRT, surface water quality

## INTRODUCTION

Water supply in South Africa is characterised by both achievements and challenges. In recent years, the country has made satisfactory progress with regard to improving access to water supply in urban areas. However, in some rural areas, women spend up to one-third of their time fetching water, and many rural dwellers are still without access to safe water sources and are compelled to take untreated water from rivers and dams. As a result of this situation, it is necessary to have a methodology which can be used for fast determination of pollutants, both organic and inorganic, which may possibly contaminate streams and wells. As water quality problems can arise very quickly, and can also be extremely short lived (e.g. spills or short-term releases into rivers), the methodology must be easy to implement, rapid to deploy, and must be sufficiently sensitive to detect the trace presence of harmful contaminants.

Spot water sampling gives chemical information specific to the moment of sampling and may fail to detect intermittent or transitory pollution. In contrast, passive sampling delivers a chemical profile representing days, weeks, or months depending on the duration of sampling. Furthermore, passive samplers accumulate analytes over time and thus provide enhanced sensitivity for trace level analytes compared to conventional bottle collection of water.

Silicone rubber (polydimethylsiloxane (PDMS)) functions as a hydrophobic solvent (Baltussen et al., 2002) and is therefore ideally suited for the in situ enrichment of persistent organic pollutants from water. Passive samplers are solvent extracted prior to instrumental analysis to obtain the trapped contaminants in an easily analysable form. Solvent extraction has the

disadvantage that it requires large amounts of often hazardous solvents and only microlitre amounts of the solvent extract are analysed. To address the disadvantages of bulk sample collection followed by solvent extraction, a cheap and easy to use passive sampler made from silicone rubber (PDMS) tubing, previously developed for solvent-free extraction of soil (Naudé et al., 2011; Naudé and Rohwer, 2012), was used. The passive sampler was applied to concentrate pollutants from surface water in and around Pretoria, South Africa. First results are reported.

## METHODOLOGY

### Sampling sites

Streams were sampled, in situ, at 3 different locations:

- Site 1: A small stream (Hartbeesspruit) flowing through the University of Pretoria (UP) recreational area, close to sports grounds, recreational braai (barbecue) areas and student residences (for 3 days)
- Site 2: The Moreletaspruit flowing through residential areas (for 3 days)
- Site 3: The Rietvleispruit running through the Rietvlei Nature Reserve (5 weeks).

The watercourses run through natural, industrial, and residential areas, and informal settlements. Sampling was performed from October 2013 to February 2014, in the summer, during the rainy season in Pretoria, South Africa.

### Miniature passive sampler

A sampling loop was fashioned by taking a 10.5 cm (0.02 g) length of silicone elastomer medical grade tubing (0.64 mm OD × 0.3 mm ID, Sil-Tec Technical Products, Georgia, USA) and joining the ends by inserting a 1 cm piece of fused silica capillary column (250 µm ID) (Fig. 1). A loop arrangement prevents water from entering the PDMS tubing and aids ease of

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**Figure 1**

*PDMS sampling loop: a 10.5 cm length of a silicone elastomer medical grade tubing joined at the ends by a 1 cm piece of fused silica capillary column*

handling. The sorption volume of the loop was 26  $\mu\text{l}$  (Naudé, et al. 2011; Naudé and Rohwer, 2012). PDMS loops were inserted into a stainless steel mesh basket (43 mm  $\times$  30 mm) (Goldsmith & Jewellery Supplies, Pretoria, South Africa). The sampling device was placed in situ, fully submerged in the watercourses described above.

After sampling, the PDMS loops were blotted with tissue paper and stored in an airtight glass container at 4°C. The isolated analytes were desorbed from the PDMS loop either in the inlet liner of a GC inlet or in a Gerstel™ thermal desorber system. Alternatively, the analytes were solvent extracted from the PDMS loop with 1 mL *n*-hexane (Merck, South Africa) followed by ultrasonication for 20 min. One  $\mu\text{l}$  of the solvent extract was injected (250°C) in the splitless mode (1 min) for analysis.

#### Thermal desorption with cooled injection

After passive sampling, the PDMS loop was inserted into a 17.8 cm long glass desorption tube (4 mm ID, 6.00 mm OD) from Gerstel™ (Chemetrix, Midrand, South Africa) for thermal desorption into a GCxGC-TOFMS. Compounds concentrated onto the PDMS sampler were thermally desorbed by heating the traps in a Gerstel™ thermal desorber system (TDS 3) from 30°C (3 min) at 60°C/min to 250°C (10 min) with a desorption flow rate of 100 mL/min at a vent pressure of 117 kPa (helium 5.0, Afrox, South Africa). The TDS transfer line temperature was 350°C. The desorbed analytes were cryogenically focused at -50°C using liquid nitrogen (Afrox, South Africa) and a cooled injection system (Gerstel CIS 4) with an empty baffled deactivated glass liner. After desorption, a splitless injection (purge on at 1 min, purge flow 40 mL/min, solvent vent mode) was performed by heating the CIS from -50°C at 10°C/s to 250°C and holding it there for the duration of the GC run.

#### Thermal desorption in a GC inlet

The PDMS loop was inserted into the glass inlet liner (splitless) of a GCxGC-TOFMS or GC-HRT and desorbed at 250°C with a splitless time of 1 min.

#### GCxGC-TOFMS

Separation of compounds was performed on a LECO Pegasus 4D comprehensive gas chromatograph – time of flight mass spectrometer (GCxGC-TOFMS) including an Agilent 7890 GC (LECO Africa (Pty) Ltd., Kempton Park, South Africa). The system included a secondary oven and a dual stage modulator. Nitrogen gas (nitrogen generator) was used for both the cold jets and the hot jets. The gas for the cold jets was cooled by passing it through a dewar filled with liquid nitrogen. The column set consisted of a 30 m  $\times$  0.25 mm ID  $\times$  0.25  $\mu\text{m}$  df Rxi 5SilMS (5% phenyl, 95% dimethylpolysiloxane) as the primary column (1D), joined to a 1 m  $\times$  0.25 mm ID  $\times$  0.25  $\mu\text{m}$  df Rxi-17Sil MS secondary column (2D) (Restek, Bellefonte, PA, USA). The primary column was connected to the secondary column with a presstight column connector (Restek, Bellefonte, PA, USA). The primary oven temperature programme was 40°C (1 min) at 10°C/min to 320°C (2 min). The GC run time was 31 min. The secondary oven was offset by +10°C from the primary oven. The modulator temperature was offset 15°C from the second oven temperature. The modulation period was 3 s with a hot pulse time of 0.6 s. The carrier gas (helium 5.0, Afrox, South Africa) flow rate was 2 mL/min in the constant flow mode. The MS transfer line temperature was set at 300°C. The ion source temperature was 230°C, the electron energy was 70 eV in the electron ionisation mode (EI+), the data acquisition rate was 100 spectra/s, the mass acquisition range was 35–520 Da, and the detector voltage was set at -1 815V. Compounds were tentatively identified based on comparison of mass spectra (match quality  $\geq$ 80%) and experimental linear retention indices (RI) to those of the National Institute of Standards and Technology (NIST08) library and literature.

#### GC-HRT

The high-resolution TOFMS system was a Pegasus HRT (LECO Corporation, St Joseph, MI, USA) using Folded Flight Path technology (Verentchikov et al., 2005). The system had an Agilent 7890 GC (Agilent Technologies, Mississauga, ON) equipped with an Agilent 4513A autosampler. The column used was a 30 m  $\times$  0.25 mm ID  $\times$  0.25  $\mu\text{m}$  df Rxi-5MS (5% phenyl, 95% dimethylpolysiloxane) (Restek, Bellefonte, PA, USA). The oven temperature programme was 35°C (1 min) at 10°C/min to 320°C (2 min). The GC run time was 31.5 min. The carrier gas (helium 5.0, Afrox, South Africa) flow rate was 2 mL/min in the constant flow mode. The MS transfer line temperature was set at 300°C. The ion source temperature was 250°C, the electron energy was 70 eV in the electron ionisation mode (EI+), the data acquisition rate was 4 spectra/s, the mass acquisition range was 45–520 Da, and the extraction frequency was 1.8 kHz. Compounds were tentatively identified based on comparison of mass spectra to those of the NIST08 library. Mass accuracy was used to determine elemental composition which provided confirmation of the library search results.

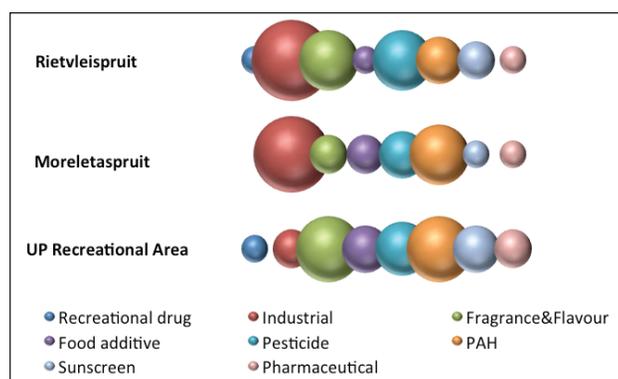
#### RESULTS AND DISCUSSION

Dissolved compounds in surface water from 3 different sites were concentrated using PDMS loops as a passive sampler, and the results are depicted in Tables 1 to 6. Rather than present the full list of compounds, data representative of different compound classes only are described in this publication. A full list of all the compounds detected is available on request from

the authors. Selected compounds detected by GCxGC-TOFMS are reported in Tables 1 to 3, and those detected by GC-HRT are reported in Tables 4 to 6. The compounds described have been chosen to show the versatility of the trapping process for common chemicals found in the environment. In addition, they indicate a difference in the composition of the river water at the different sites.

GCxGC-TOFMS is a particularly effective tool for this type of analysis, due to its superior resolving capability based on both the boiling point and the polarity of compounds. The GC-HRT provides excellent mass accuracy (routinely <1 ppm) and this feature can be used to determine elemental composition which provides good confirmation of the library search results.

Distinct profiles are observed for each of the 3 sampling points (Fig. 2). PAHs (polycyclic aromatic hydrocarbons) are commonly found in the South African environment, especially close to informal settlements and recreational areas where open fires for warmth and cooking are common. Two of the rivers also flow close to small industrial areas, and this is indicated by the presence of several industrial chemicals (Fig. 2). Pesticides and herbicides are also found where the rivers are close to agricultural areas (Fig. 2). Personal care products are evident in the water which flows through residential areas and close to student residences and informal settlements. Caffeine, an ingredient in many beverages, food and medicinal products, was detected in water from the Moreletaspruit (Site 2) (Table 5). Since caffeine is excreted in urine, its presence in the aquatic environment serves as an indicator of human pollution (Ferreira, 2005).



**Figure 2**  
Compound classes detected in surface water from the 3 sites by GCxGC-TOFMS and GC-HRT

Sample introduction into a GC-MSTOF was versatile in that the analytes were removed from the sampler device by either direct desorption in the GC inlet (GC-HRT), or by TDS (GCxGC-TOFMS), or by solvent extraction (GC-HRT). The advantage of thermal desorption, when compared to conventional liquid injection of microlitre amounts of a dilute extract, is enhanced sensitivity as the entire sample mass is transferred to the GC. A disadvantage is that thermal desorption is destructive. However, multiple loops are inserted into replicate stainless steel baskets and thus a sufficient number of loops are available for replicate runs.

Compound	Class	Similarity <sup>1</sup>	Formula	<sup>1</sup> D RT <sup>2</sup> (s)	<sup>2</sup> D RT <sup>3</sup> (s)	<sup>1</sup> D RI <sub>exp</sub>	<sup>1</sup> D RI <sub>Lit</sub> NIST08
Imidazole	Fungicide	972	C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	448	0.69	1 057	1 042, 1 069
Gamma-hydroxybutyrolactone	Recreational drug	856	C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>	386	0.96	929	924
a-Phellandrene	Fragrance	864	C <sub>10</sub> H <sub>16</sub>	398	0.48	990	1 004 <sup>4</sup>
Maltol	Flavour	935	C <sub>8</sub> H <sub>10</sub> O	498	0.76	1 093	1 091
Naphthalene	PAH	917	C <sub>10</sub> H <sub>8</sub>	564	0.81	1 195	1 197
Methenamine	Antibiotic	838	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>	614	0.84	1 269	1 273
Caprolactam	Industrial	899	C <sub>6</sub> H <sub>11</sub> NO	628	1	1 290	Not available for Rxi-5 phase
Triacetin	Food and drug additive	952	C <sub>9</sub> H <sub>14</sub> O <sub>6</sub>	690	0.75	1 379	1 344
Piperonal	Fragrance and flavour	892	C <sub>8</sub> H <sub>6</sub> O <sub>3</sub>	692	0.93	1 386	Not available for Rxi-5 phase
Ethylparaben	Antifungal Preservative Food additive	824	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	858	0.72	1 602	Not available for Rxi-5 phase
Terbutylazine	Pesticide	935	C <sub>9</sub> H <sub>16</sub> ClN <sub>5</sub>	1 008	0.85	1 857	Not available for Rxi-5 phase
Phenanthrene	PAH	954	C <sub>14</sub> H <sub>10</sub>	1 018	0.99	1 815	1 797
Anthrone	Tricyclic aromatic ketone	888	C <sub>14</sub> H <sub>10</sub> O	1 042	0.98	1 908	1 934
Homosalate	Sunscreen	914	C <sub>16</sub> H <sub>22</sub> O <sub>3</sub>	1 066	0.7	1 879	Not available for Rxi-5 phase
Thioxanthene	Pharmaceutical drug	811	C <sub>13</sub> H <sub>10</sub> S	1 088	1.01	1 977	Not available
Chlorpyrifos	Pesticide	876	C <sub>9</sub> H <sub>11</sub> C <sub>13</sub> NO <sub>3</sub> PS	1 128	0.87	1 961	1 950, 1 967
Oxybenzone	Sunscreen	922	C <sub>14</sub> H <sub>12</sub> O <sub>3</sub>	1 164	1	2 009	Not available for Rxi-5 phase

<sup>1</sup>Spectral match quality (NIST08 library)

<sup>2</sup>First dimension retention time

<sup>3</sup>Second dimension retention time

<sup>4</sup>Babushok et al. (2011)

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TABLE 2 Selected compounds found in water from the Moreletaspruit by GCxGC-TOFMS							
Compound	Class	Similarity <sup>1</sup>	Formula	<sup>1</sup> D RT <sup>2</sup> (s)	<sup>2</sup> D RT <sup>3</sup> (s)	<sup>1</sup> D RI <sub>exp</sub>	<sup>1</sup> D RI <sub>Lit</sub> NIST08
2,3-Butanedione (Diacetyl)	Flavour	801	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	118	0.35	618	608, 621
2-Furancarboxitrile	Sweetening agent	927	C <sub>5</sub> H <sub>3</sub> NO	212	0.58	669	Not available
Ethylbenzene	Industrial Petrochemical	877	C <sub>8</sub> H <sub>10</sub>	264	0.49	812	833
p-Xylene	Industrial Petrochemical	944	C <sub>8</sub> H <sub>10</sub>	272	0.5	823	848
Styrene	Industrial	935	C <sub>8</sub> H <sub>8</sub>	290	0.55	847	857
Hexylene glycol	Industrial Washing/cleaning products	917	C <sub>6</sub> H <sub>14</sub> O <sub>2</sub>	330	0.58	900	892
Benzaldehyde	Industrial Flavour	937	C <sub>7</sub> H <sub>6</sub> O	356	0.73	935	926
Limonene	Flavour Personal care	939	C <sub>10</sub> H <sub>16</sub>	420	0.5	1 020	1 017
Biphenyl	Industrial Pesticide	913	C <sub>12</sub> H <sub>10</sub>	726	0.8	1 427	1 425
Fluorene	PAH	931	C <sub>13</sub> H <sub>10</sub>	882	0.89	1 634	1 604
9H-Xanthene	Fungicide	863	C <sub>13</sub> H <sub>10</sub> O	908	0.85	1 669	1 661
Dibenzothiophene	Petroleum	896	C <sub>12</sub> H <sub>8</sub> S	998	0.99	1 788	1 766
2-Ethylhexyl salicylate	Sunscreen	854	C <sub>15</sub> H <sub>22</sub> O <sub>3</sub>	1 026	0.65	1 826	Not available
Fluoranthene	PAH	938	C <sub>16</sub> H <sub>10</sub>	1 186	1.07	2 038	2 039
Pyrene	PAH	932	C <sub>16</sub> H <sub>10</sub>	1 216	1.14	2 078	2 072

<sup>1</sup>Spectral match quality (NIST08 library)

<sup>2</sup>First dimension retention time

<sup>3</sup>Second dimension retention time

TABLE 3 Selected compounds found in water from the Rietvleispruit by GCxGC-TOFMS							
Compound	Class	Similarity <sup>1</sup>	Formula	<sup>1</sup> D RT <sup>2</sup> (s)	<sup>2</sup> D RT <sup>3</sup> (s)	<sup>1</sup> D RI <sub>exp</sub>	<sup>1</sup> D RI <sub>Lit</sub> NIST08
1,3-Butanediol	Solvent Food flavour agents	912	C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	286	0.61	842	Not available
Dimethyl trisulfide	Bacterial decomposition	868	C <sub>2</sub> H <sub>6</sub> S <sub>3</sub>	362	0.68	943	950
Phenol	Industrial Herbicides Pharmaceutical Petroleum	930	C <sub>6</sub> H <sub>6</sub> O	372	0.66	956	961
Benzonitrile	Industrial	861	C <sub>7</sub> H <sub>5</sub> N	376	0.76	961	951, 986
Benzyl chloride	Industrial	846	C <sub>7</sub> H <sub>7</sub> Cl	404	0.68	999	1 002
Phenylethyl alcohol	Fragrance	944	C <sub>8</sub> H <sub>10</sub> O	498	0.76	1 123	1 113
Quinoline	Coal Environmental contaminant	923	C <sub>9</sub> H <sub>7</sub> N	612	0.88	1 275	1 247
Hydroquinone	Skin whitening (banned)	809	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	632	0.91	1 302	1 327
(E)-Cinnamaldehyde	Flavour and fragrance Fungicide	916	C <sub>9</sub> H <sub>8</sub> O	638	0.86	1 310	1 323
Phthalimide	Plastic	949	C <sub>8</sub> H <sub>5</sub> NO <sub>2</sub>	792	1.05	1 514	Not available
Diethyltoluamide (DEET)	Insect repellent	932	C <sub>12</sub> H <sub>17</sub> NO	870	0.84	1 618	Not available for Rxi-5 phase

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Compound	Class	Similarity <sup>1</sup>	Formula	<sup>1</sup> D RT <sup>2</sup> (s)	<sup>2</sup> D RT <sup>3</sup> (s)	<sup>1</sup> D RI <sub>exp</sub>	<sup>1</sup> D RI <sub>Lit</sub> NIST08
Fluorene	PAH	934	C <sub>13</sub> H <sub>10</sub>	882	0.88	1 634	1 595
Terbuthylazine	Herbicide	902	C <sub>9</sub> H <sub>16</sub> ClN <sub>5</sub>	1 006	0.85	1 799	1 778
Metalochlor	Herbicide	853	C <sub>15</sub> H <sub>22</sub> ClNO <sub>2</sub>	1 124	0.86	1 956	1 968
Oxybenzone	Sunscreen	889	C <sub>14</sub> H <sub>12</sub> O <sub>3</sub>	1 162	1	2 007	Not available for Rxi-5 phase

<sup>1</sup>Spectral match quality (NIST08 library)

<sup>2</sup>First dimension retention time

<sup>3</sup>Second dimension retention time

Compound	Class	RT <sup>1</sup> (s)	Similarity <sup>2</sup>	Formula	Mass accuracy (ppm)
2-Furanone	O	332	548	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub>	-0.93
2-Pentylfuran	Flavour	405.3	822	C <sub>9</sub> H <sub>14</sub> O	-0.15
1,3,5-Trimethylbenzene	Combustion VOC <sup>3</sup>	407.3	889	C <sub>9</sub> H <sub>12</sub>	-0.08
1,2-Dichlorobenzene	Cl	425.4	783	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	-0.44
Limonene	Personal care Flavour	442.3	638	C <sub>10</sub> H <sub>16</sub>	0.01
1-Ethyl-2,4-dimethylbenzene	Aromatic	488.8	861	C <sub>10</sub> H <sub>14</sub>	-0.53
o-Cymene	Personal care	495	623	C <sub>10</sub> H <sub>14</sub>	0.08
Dodecane	Hydrocarbon	597.3	712	C <sub>12</sub> H <sub>26</sub>	1.89
Benzothiazole	S	622.8	853	C <sub>7</sub> H <sub>5</sub> NS	-0.44
Indole	N	680.5	632	C <sub>8</sub> H <sub>7</sub> N	-0.7
Acenaphthene	PAH	832.3	653	C <sub>12</sub> H <sub>10</sub>	-0.55
Dibenzofuran	O	855.5	857	C <sub>12</sub> H <sub>8</sub> O	-0.32
1H-Phenylene	PAH	904	571	C <sub>13</sub> H <sub>10</sub>	0.74
Bifenthrin	Pesticide	932.3	603	C <sub>14</sub> H <sub>13</sub>	-0.48
Benzophenone	Sunscreen additive	934	820	C <sub>13</sub> H <sub>10</sub> O	-1.08
Dibenzothiophene	S	1 018.5	840	C <sub>12</sub> H <sub>8</sub> S	0.27
Anthracene	PAH	1 035.8	925	C <sub>14</sub> H <sub>10</sub>	0.05
Pyrene	PAH	1 204.3	943	C <sub>16</sub> H <sub>10</sub>	1.9
Benz[a]anthracene	PAH	1 411	912	C <sub>18</sub> H <sub>12</sub>	-0.05
Perylene	PAH	1 550.3	806	C <sub>20</sub> H <sub>12</sub>	0.23

<sup>1</sup>Retention time

<sup>2</sup>Spectral match quality (NIST08 library)

<sup>3</sup>Volatile organic compound

Compound	Class	RT (s)	Similarity	Formula	Mass accuracy (ppm)
2-Cyclohexen-1-one	O	336.8	785	C <sub>6</sub> H <sub>8</sub> O	0.41
Phenol	Industrial chemical	391.8	774	C <sub>6</sub> H <sub>6</sub> O	0.21
Benzothiazole	S	613	530	C <sub>7</sub> H <sub>5</sub> NS	-0.41
Vanillin	Food additive	755.8	846	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	-0.45
Diphenyl ether	Industrial chemical	758.8	532	C <sub>12</sub> H <sub>10</sub> O	0.02
Dimethyl phthalate	Plasticiser	787.7	891	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	-0.55

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Compound	Class	RT (s)	Similarity	Formula	Mass accuracy (ppm)
Cyclodecane	Hydrocarbon	809.3	776	C <sub>10</sub> H <sub>20</sub>	0.75
Benzylbenzoate	Plant constituent	1 015.3	823	C <sub>14</sub> H <sub>12</sub> O <sub>2</sub>	-0.86
Anthracene	PAH	1 027.5	834	C <sub>14</sub> H <sub>10</sub>	0.5
Caffeine	Stimulant	1 065.9	570	C <sub>8</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>	2.65
Fluoranthene	PAH	1 196.3	677	C <sub>16</sub> H <sub>10</sub>	-0.29
Methyl stearate	FAME <sup>1</sup>	1 222	795	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	-2.58
Flusizilazole	Fungicide	1 271.9	768	C <sub>16</sub> H <sub>15</sub> F <sub>2</sub> N <sub>3</sub> Si	-3.26

<sup>1</sup>Fatty acid methyl ester

Compound	Class	RT (s)	Similarity	Formula	Mass accuracy (ppm)
3-Methyl-2-butanone	Solvent	175.1	712	C <sub>5</sub> H <sub>10</sub> O	0.1
3-Hexanone	Solvent	222.5	977	C <sub>6</sub> H <sub>12</sub> O	0.74
p-Xylene	Industrial chemical	289.3	845	C <sub>8</sub> H <sub>10</sub>	0.77
2,5-Hexanedione	Diketone	583	904	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>	1.16
Benzaldehyde	Flavourant	584	926	C <sub>7</sub> H <sub>6</sub> O	-0.62
Butyrolactone	Recreational intoxicant	668.8	852	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	1.18
2-Furanmethanol	Industrial chemical	692.3	640	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	1.42
2-Decen-1-ol	Flavour and fragrance	725	798	C <sub>10</sub> H <sub>20</sub> O	-2.02
Diethylphthalate	Plasticiser	1 119.6	916	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>	-1.14
2-Ethylhexyl trans-4-methoxycinnamate	Sunscreen and lip balm	1 155.5	741	C <sub>18</sub> H <sub>26</sub> O <sub>3</sub>	-0.3
5-Hydroxymethylfurfural	Food constituent	1 187.4	656	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	1.79
Fluoranthene	PAH	1 199.3	943	C <sub>16</sub> H <sub>10</sub>	-0.23
Pyrene	PAH	1 326.5	916	C <sub>16</sub> H <sub>10</sub>	-0.02
4-Hydroxybenzaldehyde	Flavourant	1 403.3	746	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	-0.07

In this study, the passive sampler was employed as an inexpensive and simple pollutant screening tool. However, contaminant concentrations may be derived by using performance reference compounds to determine in situ passive sampler sampling rates followed by conversion into water concentration of the analytes by means of silicone rubber specific partition coefficients (Yates et al., 2007; O'Hara, 2009; Booij and Smedes, 2010; Monteyne et al., 2013). The silicone rubber tubing passive sampler as a quantitative device will form part of a follow-up study.

Commercial passive samplers can be expensive (ITRC, 2005). In contrast, the miniature passive sampler was cheap, with the cost of manufacturing per sampler less than ZAR35 (ZAR7 for the sampling loop + ZAR25 for the stainless steel mesh basket). The passive sampler requires a minimum of storage space and can withstand transport over rough terrain which is not always the case for glass sample bottles.

## CONCLUSIONS

The PDMS passive sampling device was cheap and easy to use. Enhanced sensitivity was achieved by solvent-free sample introduction. Each sampling site exhibited a different chemical

profile depending on the source of input. Contaminants detected in surface water included caffeine, personal care products, pharmaceuticals, pesticides and PAHs.

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