



Figure SI1: Evidence of pollution along the Msunduzi River at DuTV Bridge (26 May 2014).

Quality assurance of analysis

To evaluate the efficiency of the extraction of the targeted PAHs and their detection by GC-MS, samples of water, soils and surface sediments in duplicates were spiked with known amounts of the 7 PAH standards, and left to equilibrate for 2 days. The un-spiked and the equilibrated spiked split portions were extracted as described in the experimental section and analysed by GC-MS. Examples of Total Ion Chromatograms (TICs) for extracts of spiked samples are shown in Figures S2 and S3.

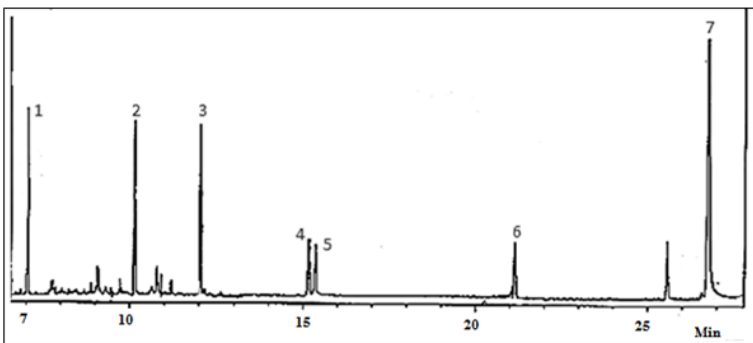


Figure SI2: A TIC recorded for an extract of spiked sediment (collected from the Agricultural Area (AA)) during the autumn of 2014, where 1=Naphthalene, 2=Acenaphthylene, 3=Fluorene, 4=Phenanthrene, 5=Anthracene, 6=Pyrene and 7=Chrysene.

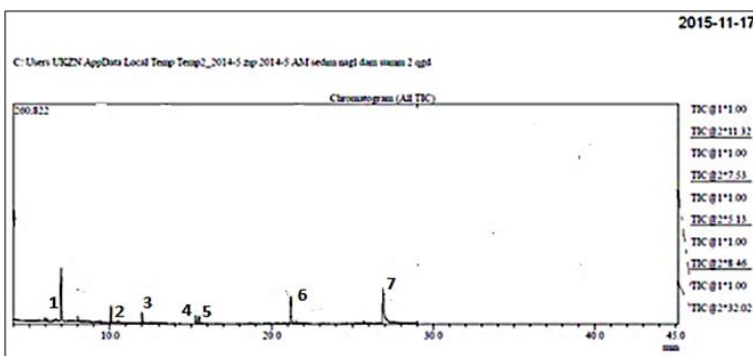


Figure SI3: TIC of an extract of water from the NDA sampling site during the summer of 2014, where 1=Naphthalene, 2=Acenaphthylene, 3=Fluorene, 4=Phenanthrene, 5=Anthracene, 6=Pyrene and 7=Chrysene.

PAHs	Retention times (minutes)	M.W. (g/mole)	Confirmation ions (m/z)
NA-d8	6.95	136	136
NA	6.96	128	128; 127
ACY	10.01	152	152; 151
FLUO	11.93	166	166; 165
PHEN	15.22	178	178; 176
ANTH	15.41	178	178; 89
PYR	21.08	202	202; 101
CHRY	26.78	228	226; 228

Table SI1: TIC, retention times and confirmation m/z values of analysed PAHs, where NA-d8=Naphthalene-d8, NA=Naphthalene, ACY=Acenaphthylene, FLUO=Fluorene, PHEN=Phenanthrene, ANTH=Anthracene, PYR=Pyrene and CHRY=Chrysene.

PAHs	LOD distilled water (ng/L)	LOQ distilled water (ng/L)	LOD soil blank (ng/g)	LOQ in solid samples (ng/g)	Recovery in spiked sediments (%)	Recovery in spiked river water (%)	R ²
NA	0.5	1.02	0.55	1.01	79.16 ± 0.01	99.66 ± 0.14	0.9996
ACY	0.72	1.07	0.7	2.4	99.10 ± 0.02	95.77 ± 0.32	0.9985
FLUO	0.77	1.01	0.36	1.06	95.19 ± 0.01	105.56 ± 0.01	0.9995
PHEN	0.34	1	0.4	1.07	83.79 ± 0.65	80.35 ± 0.05	0.9955
ANTH	0.61	1.05	0.12	2.21	98.59 ± 0.21	92.15 ± 0.01	0.999
PYR	0.4	1.1	0.38	1.04	95.56 ± 0.03	80.30 ± 0.02	0.9995
CHRY	0.27	1.31	0.3	1.05	101.28 ± 0.02	96.15 ± 0.01	0.9985

Table SI2: LODs and LOQs (for extracts of distilled water and uncontaminated soil) and % recoveries of 7 PAHs from spiked sediments and water. LOD is the Limit of Detection and LOQ is the Limit of Quantification at 3 and 10 times the standard deviation of a reagent/ field blank.

Seasons	Parameters	Sampling sites								
		HD	CD	DuTV	DWWTP Inlet	DWWTP Outlet	AA	MT	JUM	NDA
Autumn of 2014	pH of water	7	6.65	6.31	5.67	6.7	5.86	8.1	5.72	7.71
	Conductivity ($\mu\text{S}/\text{cm}$) at 25°C	103.8	187.9	144.1	655	698	279	348	30	91.8
	Water T (°C)	16.8	16.6	17.8	23	24	18.3	18.7	18.3	20.1
	Ambient T (°C)	28.2	25.3	25.5	29.3	29.2	29.2	21.6	18.3	24.1
Winter of 2014	pH of water	7.99	7.85	7.79	7.34	7.39	8.69	9.02	8.84	7.8
	Conductivity ($\mu\text{S}/\text{cm}$) at 25°C	120.4	225	169.6	946	703	387	435	318	90.3
	Water T (°C)	12.9	16.3	19.9	22.2	16.7	17.8	19.3	19.5	20.3
	Ambient T (°C)	26.6	31	32.5	21.1	21.4	33.8	34.7	33.3	30.4
Summer of 2014	pH of water	7.6	7.42	7.39	7.39	7.77	7.68	7.88	8.1	8.33
	Conductivity ($\mu\text{S}/\text{cm}$) at 25°C	83.9	132.9	125.2	865.5	543	300.3	329	279.5	105.6
	Water T (°C)	25	27.1	23.1	28.7	27.7	27.9	27.8	27.2	28.7
	Ambient T (°C)	27.5	29	31.8	31.4	31.4	32.8	37.7	33	37
Spring of 2015	pH of water	6.78	7.79	7.67	7.21	7.37	8.64	8.32	6.74	8.54
	Conductivity ($\mu\text{S}/\text{cm}$) at 25°C	103.7	384.2	267.2	1165	928.2	253.5	231.7	355.7	119
	Water T (°C)	15.3	21.5	16.2	19.7	16	25	17.9	20	26.2
	Ambient T (°C)	16.3	17.1	18.4	16.1	20.6	25.2	19.5	26.8	28.5

Table SI3: Physical parameters of the Msunduzi River water.

Extraction of PAHs in water samples

Liquid-liquid extraction of PAHs from the water and the wastewater samples: A 50 ml aliquot of DCM (chromatographic grade) was added to 500 ml of river water/wastewater, in a separating funnel. Naphthalene-d8 (25 ml, 100 mg/L) was also added to the mixture as a surrogate standard. The mixture was shaken for a period of 30 minutes with intermittent release of pressure. This allowed enough contact between the PAHs in the aqueous phase and the collecting organic solvent.

The two phases were allowed to separate out before the organic layer was collected into a receiving flask. Two more aliquots (30 ml and 20 ml, respectively) were added to the spent portion of the water and the extraction process was repeated.

The combined organic layers were dried with 20 g of Sodium sulphate anhydrous and filtered. The volume of the dried extracts was reduced to 5 ml using a rotary vacuum evaporator (Laborota 4000 Eco, Heidolph) and purified as described for soils and sediments.

Pre-treatment of soils and sediments and Soxhlet extraction of PAHs: The soils and surface sediments were removed from the fridge and spread on Aluminium foils and left to air-dry in a dark room. The dried soils and surface sediments were screened through a 2 mm sieve to

initially remove debris and plant material. The segregated subsamples were then pulverized with a mortar and pestle to pass through a less than 150 μm sieve. The powders were kept in amber glass bottles that had been pre-soaked in 10% HNO_3 and rinsed with distilled water and n-hexane.