Naphthalene, a polycyclic aromatic hydrocarbon (PAH), was detected and quantified in the selected varieties of fishes collected from the Bangsai river, one of the contaminated rivers located at Savar near the Dhaka Export Processing Zone (DEPZ), Bangladesh, during the period October 2009. Naphthalene, a carcinogenic compound, was analyzed by GC–MS as it was in the mixture of dichloromethane–hexane (1:1) crude extract of the flesh of fish samples collected from the aforesaid river. A suitable and reliable procedure for the extraction of naphthalene from the fish sample has been developed. A multi-layer clean-up (silica gel) column was used, followed by glass fiber filter (GFF) paper to eliminate the interfering organic compounds as well as the lipids and fat. It was observed that PAHs deposition on the samples takes place in different morphological parts of the biological materials. The PAH, naphthalene, was found in almost all of the fish samples and the concentration of which was in the range 0.030–1.004 μg/g. Recovery studies with fortified samples indicated that the recovery efficiency for naphthalene was about 79.14%. This concentration is within the range of values reported for other comparable regions of the world.