The authoritative version of this manuscript can be found in the Wiley journal *Water and Environment Journal* here. Full citation details:

White, K. J., Mayes, W. M. and Petrovan, S. O. (2017), Identifying pathways of exposure to highway pollutants in great crested newt (*Triturus cristatus*) road mitigation tunnels. *Water and Environment Journal*. DOI: 10.1111/wej.12244

# Identifying pathways of exposure to highway pollutants in great crested newt (*Triturus cristatus*) road mitigation tunnels


## AUTHORS

Katie J. White BSc., School of Environmental Sciences, University of Hull, UK

William M. Mayes PhD., CEnv., FRGS., School of Environmental Sciences, University of Hull, UK, corresponding author: w.mayes@hull.ac.uk, +44(0)1723357292.

Silviu O. Petrovan PhD. Conservation Coordinator, Froglife, Peterborough, UK and Research Associate, Conservation Science Group, Department of Zoology, University of Cambridge, Cambridge CB2 3QZ, UK.



## ABSTRACT

Road mitigation tunnels are increasingly deployed for amphibians but very little is known about chemical pollution in such schemes. We assessed pollution pressures associated with road runoff at a major great crested newt mitigation scheme in England. Sediments and waters in the mitigation system were analysed for major physico-chemical parameters, trace metals and total petroleum hydrocarbons and compared to a nearby reference site. Seven out of eight tested metals including copper, zinc, lead and iron were in significantly greater concentrations in the tunnels than at a reference site and at environmentally-significant concentrations. Water samples also exhibited elevated concentrations of aluminium and chromium and occasionally extreme alkaline pH associated with leaching of portlandite in tunnel cements. High conductivity values in waters and sediments corresponding with seasonal de-icing salt application were also apparent. The study highlights the potential pollutant pressures for amphibians associated with large-scale urban development and road mitigation schemes.



Keywords: urban pollutants, road runoff, road mitigation; trace metals, de-icing salts, amphibian

## INTRODUCTION

Road networks and road traffic have increased substantially across the globe and are significantly impacting amphibian populations (Beebee, 2013; Petrovan and Schmidt, 2016). In Europe, populations of great crested newts (*Triturus cristatus)* have suffered severe declines due to habitat loss and fragmentation as a result of urbanisation and intensification of agricultural practices (Langton *et al.,* 2001). Some amphibian declines are also attributed globally to environmental pollution (Egea-Serrano *et al.*, 2012). Pollutants of particular concern include chemical pesticides and fertilisers (Langton *et al.*, 2001), as well as trace metals, road de-icing salts and hydrocarbons (Duff *et al*. 2010; Sparling *et al.,* 2010).

In the UK, *T. cristatus* are protected by national and European legislation including the EU Habitats Directive (European Council Directive 92/43/EEC) and the Wildlife and Countryside Act 1981. Like other amphibians, *T. cristatus* require a combination of aquatic and terrestrial habitat for foraging, overwintering and breeding. Also, *T. cristatus* typically form metapopulations where there are pond clusters and it is essential for their long-term conservation that they can navigate between habitat patches and ponds to forage for resources, breed and prevent narrowing of the gene pool (Edgar and Bird, 2006). Short-distance migrations of newts towards breeding sites (ponds) normally occur in early spring (March-April), while the longer distance dispersal movements mostly occur during autumn months (September-November). As part of ecological mitigation, road underpasses may be installed to allow newt movements between ponds or between aquatic and terrestrial habitat, especially when newly-constructed roads fragment their habitats. Such road underpasses are increasingly implemented in Europe as connectivity mitigation around urban and suburban developments. However, given the resultant proximity of the amphibian habitat to a source of potential aquatic pollutants- roads (Van Boheman and Van De Laak, 2003), and the sensitivity of amphibians to many common pollutants (due to their permeable skin), there are concerns that road tunnels may act as a pathway to exposure of amphibians to road-related pollutants. Typical pollutants associated with road runoff consist of trace metals, de-icing salts in winter and petroleum and diesel hydrocarbons (Bäckström et al, 2003). Metal issues usually focus on those sourced from general vehicle wear, e.g. copper and zinc from brake pads, and the latter additionally from tyre wear and corrosion of galvanized safety barriers (Legret and Pagotto,1999). In addition, there may be stark seasonal and event-based changes in pollutants associated with seasonal application of deicing salts and first flush episodes respectively (Legret and Pagotto, 1999; Lee *et al.,* 2002). Contaminants may reach the tunnels and aquatic habitat through runoff, road splash or through dry deposition in particulate form (Bäckström et al, 2003); thus there are several pathways by which the pollutants could accumulate in the habitat and impact the population. This study aims to provide an initial assessment of potential pollutant exposure in newt mitigation tunnels at a major urban development in England and to use this as a case study.

We hypothesised that there would be no significant difference in contaminant concentrations or major physico-chemical parameters between sediment samples collected from amphibian mitigation tunnels and those from reference sites.

## METHODS

### *Study site*

The study site was a mitigation scheme constructed in 2014 in England adjacent to a major retail development. As part of the ecological mitigation, given the discovery of a medium-sized population of *T. cristatus*, a new wetland habitat was created away from the construction site and exclusion from the development was ensured with amphibian fencing according to standard practices (Natural England, 2015). Three other amphibian species were also present and use the tunnels, plus the protected European otter (*Lutra lutra*). Two pairs of polymer-concrete amphibian climate tunnels (ACO, Germany) were installed underneath a newly constructed main access road to enable the newts to safely navigate between ponds to forage and breed. These widely-used tunnels have open slots into the road surface, allowing free air and humidity circulation in an effort to minimise microclimate differences which could reduce amphibian usage. The western entrances to the tunnels are adjacent to areas of terrestrial habitat and pondscapes, with the eastern side adjoining terrestrial habitat and a newly-constructed Sustainable Urban Drainage System (SUDS; Figure 1). The area is mostly suburban and the site lies on clays and silts of Quaternary age. The reference site was 6 km from the development, in a similar lowland area with a mix of both terrestrial and aquatic habitats, similar topography and similar superficial geology; the key difference being that it was away from any potential road pollutant sources.

### *Sampling and analysis*

Between 12 and 18 bulk sediment samples were taken from tunnel entrances and road surfaces in January, March and November 2015 and March 2016 depending on availability of material to sample. Samples were taken from the concrete aprons of the 4 different tunnel entrances at the site and consisted of up to 500g bulk sample and placed in polythene sample bags. Six reference samples were taken on each occasion from the nearby reference site. Sediment conductivity and pH were determined in the laboratory using standard soil paste methods (1:5 dilution with deionised water: ISO, 2005) and measurement on a frequently-calibrated Myron Company Ultrameter. Organic content of sediments was determined by loss on ignition at 450°C until a constant weight was achieved. Air-dried sediment samples were homogenised using a pestle and mortar, disaggregated then sieved (<2mm) prior to elemental analysis using a Niton XL3t XRF analyser (Thermo Scientific, 2007). Standard certified reference materials were utilised to ensure accuracy of readings, with all readings within 10% of prescribed values. Five tunnel and 5 reference replicates collected in spring 2016 were analysed for total petroleum hydrocarbons (TPH) using gas chromatography with a flame ionisation detector (GC-FID) by ESG Ltd.

Where ponded water was apparent by the tunnel entrances in November 2015 and March 2016, major physico-chemical parameters (pH, conductivity, temperature) were analysed in the field using a Myron Ultrameter calibrated on day of sampling. Filtered (0.45μm) and total dissolved water samples were taken from selected locations for elemental content using a Perkin Elmer Optima 5300 DV Inductively Coupled Plasma-Optical Emission Spectrometer.

Data were not normal even after log transformation (Kolmogorov Smirnov p>0.05) so non-parametric methods were used to test differences in median contaminant concentrations and major physico-chemical parameters between tunnel and reference sites and between seasons at the tunnel sites (Mann-Whitney U-test). The geochemical code Phreeqc v. 3.3.3. was used to determine saturation indices for a range of mineral phases in water samples (Parkhurst and Appelo, 1999).

## RESULTS

*Sediments*

Median sediment pH in the tunnels was 8.4; significantly greater than at the reference site which had a median of 6.2 (Mann-Whitney U, W = 1258, df = 51, P = <0.001). Electrical conductivity values were significantly greater in the tunnel sediments than at the reference site (Mann-Whitney U, W = 1192 df = 51, P = 0.001) (Figure 2). The conductivity data was the only parameter that demonstrated a significant seasonal fluctuation, with significantly higher conductivity values in the tunnels in winter months (January and March: median of 630μS/cm) than autumn months (November: median of 270μS/cm), prior to the main period of deicing salt application (Figure 3). Organic content of the sediments did not differ between reference and tunnel sites (Mann Whitney: P>0.05). However, significant differences were apparent in elemental composition of the sediments (Figure 4). Tunnel sediments were typically more mineral rich, with significantly greater concentrations of Ca, K, Ti and Fe than reference sites (P: <0.001 to 0.005, Table 1, Figure 2). Of the trace elements of potential concern that were above detection limits, Cu, Mn, Pb and Zn were all apparent at significantly higher concentrations in the tunnel sediments than at reference sites (P<0.001, Figure 4). Cd, Cr and V were below detection limits (10, 30 and 40 ppm respectively) in all sediment samples. Replicate samples of loose sediment on the road surface in the vicinity of the tunnels showed a very similar composition to the tunnel sediments with high mineral content (Ca, K, Fe, Ti), electrical conductivity and elevated metal content (Cu, Mn, Pb, Zn).

Of the sub-samples analysed for Total Petroleum Hydrocarbons, similar patterns were apparent to the metals with a significantly higher TPH content in tunnels than the reference site (Mann-Whitney U, W = 40, df = 5, P = 0.01; Figure 4). The tunnels had a median TPH content of 406mg/kg (range 136-2220mg/kg) and most of these carbon molecules were longer-chained (>C21 – C35) (Supplementary Information). The reference site had a median TPH content of 41mg/kg (range 35 to 53 mg/kg).

*Water quality*

The water quality data revealed some notable patterns with regard to high sodium levels (particularly in winter) in road surface samples and elevated pH at tunnel sites which is coincident with metal enrichment (notably Al, Cr and Se: Table 2). The tunnels also showed Na concentrations above surrounding SUDS samples and consistent with mixing of road surface waters with SUDS/pondscape waters (Table 2). The higher dissolved metal concentrations of oxyanion-forming metals would be anticipated with the high pH. These highly alkaline tunnel sites were also characterised by white secondary precipitates on the substrate. Very high calcium concentrations were apparent (Table 2), while geochemical modelling of the waters suggest that this site was supersaturated with respect to calcite ($CaCO_3$; Table 2). The surrounding SUDS water quality samples did not reveal any notable pollutant pressures and are general suitable for aquatic life and typical of lowland settings (Oldham et al. 2002).

## DISCUSSION

The sediment and water analyses revealed that the null hypothesis of no significant difference in potential contaminants between mitigation tunnels and reference conditions can be rejected. A series of pollution pressures were apparent, including metal enrichment, salinity, extremely alkaline pH and potential enrichment of petroleum-related organics.

There were significantly higher concentrations ($P<0.001$ to 0.005) of trace metals in the tunnels for 7 of the 8 tested elements (Cu, Zn, Pb, Fe, Mn, Sr and Ti) compared to the reference site, which was a more rural area with a greater distance from major roads, unlike the tunnels which were underneath a main access road. It is probable that the road was the primary source of contamination as these metals are associated with road runoff (Ward, 1990). Moreover, the elements found in elevated concentrations in the tunnels were found in even greater concentrations in road surface dusts (Table 1), which suggests a clear pathway of movement. This is most likely due to surface runoff via the vents in the roof of the mitigation tunnels, or dry deposition of particulates (Bäckström *et al.,* 2003). The build-up of surface particulates at kerb edges close to tunnel vents was apparent on sample visits.

The road-affiliated pollutants were likely sourced from the motor vehicles themselves; Cu and Zn particulates may be deposited with brake disc and tyre wear (Ward,1990; Legret and Pagotto,1999) and others, such as aluminium, may have petrogenic sources (Brown and Peake, 2006). Some elements may additionally be sourced from wear of the concrete tunnels themselves or road surfaces, where industrial residues such as blast furnace slags are often used in surfacing (Mahieux *et al.,*2009). The markedly higher Ca concentrations and pH at tunnel sites are consistent with weathering of alkaline construction materials (Figure 2).

Metals of concern that appear to be present in the newt tunnels and surface water include Cu, Zn, Pb, Fe and Mn. Guidance for toxicity thresholds of metals in sediments are not well established, although the Threshold and Predicted Effects Level (TEL and PEL) guidance have been informally used as a screen in many UK settings (UKTAG, 2006). Most metals of interest (e.g. Cu, Pb and Zn) were above the lower Threshold Effects Level (above which negative effects on sediment dwelling organisms may be expected) and generally within the higher PEL values (above which negative impacts on aquatic biota may be expected: Figure 4). While some reference sites were also above the lower TEL value, possibly owing to mineral enrichment in superficial deposits given glacial and fluvial transport of sediments from adjacent areas of mineralisation (Dunham & Wilson, 1990), metal concentrations were significantly higher in the tunnels (Figure 4) than reference sites. More refined analyses on metal bioavailability would be desirable in the future to formulate more robust risk assessments. The water samples suggest enrichment of Al and Cr in particular where there is a very high pH (Table 2). Encouragingly, Zn and Cu did not exceed quality standards in freshwater samples although negative effects of dissolved zinc on amphibians at levels below quality standards have been observed (Lefcort *et al.,* 1998). Amphibians are particularly sensitive to trace metals due to their permeable skin and thin epidermis (Hopkins *et al.,* 2013).

The pH of both the sediment and water samples from tunnels were high; with one extreme reading of 11.3 reported at one of the tunnel entrances. Such alkalization of surface waters is uncommon naturally, but is widely reported as a product of weathering of alkalinity generating minerals such as portlandite ($Ca(OH)_2$) in concrete (Gomes et al., 2016). In this case, leaching of such minerals from tunnels and road ballast is likely (Nodvin *et al.,*1986) and is consistent with the supersaturation with respect to calcite (Table 2). *T. cristatus* are generally found in pH ranges of 4.4-9.5 (Langton *et al.*, 2001); thus the extreme pH of 11.3 is much greater (100 times higher) than the documented *T. cristatus* range of tolerance. Such extreme pH could be of significance to amphibians due to elevated ionic strength, elevated hydroxide concentrations (Fominykh, 2008) as well as potential indirect effects of increased mobility of oxyanion-forming contaminants, such as Cr (Table 2), which would be expected in hexavalent form at such a pH (Takeno, 1996). The area of high pH water at this site was relatively small, which should limit potential exposure, however, relatively little is known about the tolerance of amphibians to extremely alkaline waters (Fominykh, 2008).

Overall, conductivity was much greater in the tunnels than at the reference site (Figure 2). The proximity to the road suggests that the elevated conductivity is a result of seasonal de-icing salt application on the road; a notion supported by the significantly higher conductivity in March (post de-icing salt application) than in November (pre de-icing salt application) (Figure 3). Water samples had higher conductivities than the sediment (Table 2). The greatest was water at the roadside (S3) in March 2016 which was an extreme of 10,200μS/cm and extreme Na concentrations (1189mg/L); indicative of the presence of de-icing salts. Deicing salts pose serious ecological risks to amphibians due to the salinity increases and direct toxicity of chloride (Hopkins *et al.,*2012; Duff et al., 2010). Salts can have extreme adverse effects on amphibians at all life stages (Hopkins *et al.,* 2012); though embryonic and larval life stages are more sensitive than adults (Turtle, 2000).

Total petroleum hydrocarbon concentrations were significantly greater in the tunnels than the reference site ($P = 0.01$, Figure 4). Though the presence of more hydrocarbons in the tunnels does not categorically show that they are of petroleum origin (as analysis is subject to interference from organic matter and chlorinated solvents: Villalobos *et al.,* 2008), the existence of many long chain molecules is indicative of this. However, as a preliminary screen it warrants further attention, given the obvious pollution pathway in this case. Very little research has been done on the impacts of petroleum hydrocarbons on amphibians, although there is evidence that petroleum contamination of freshwater habitats has negative impacts on tadpole growth and unsuccessful metamorphosis of the anuran *Hyla cinerea* (Mahaney, 1994).

## CONCLUSIONS AND MANAGEMENT CONSIDERATIONS

1. A series of pollutant pressures on amphibian populations using road mitigation tunnels were identified.
2. These include trace metals, hydrocarbons, de-icing salts and extreme alkaline pH contaminating different features of the habitat including the tunnels themselves and surface water.
3. The exact risks posed by these potential pathways remain unclear, but the relatively limited research conducted in this area suggests that impacts could be adverse and need highlighting in planning and design of mitigation schemes for amphibians, and great crested newts in particular.
4. Further research is needed to assess the exact exposure of amphibians to the contaminants at this and other sites and should incorporate more refined assessments of metal bioavailability (e.g. metal speciation) integrated with amphibian tunnel usage data (i.e. seasonality and exposure times).

## ACKNOWLEDGEMENTS

Laurence Jarvis is thanked for assisting in sample collection. SOP is grateful for funding at Froglife by the Esmée Fairbairn Foundation under grant NR 14-0534.

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FIGURES AND TABLES

Figure 1. Location of the sample site showing sampling locations and the amphibian mitigation tunnels.

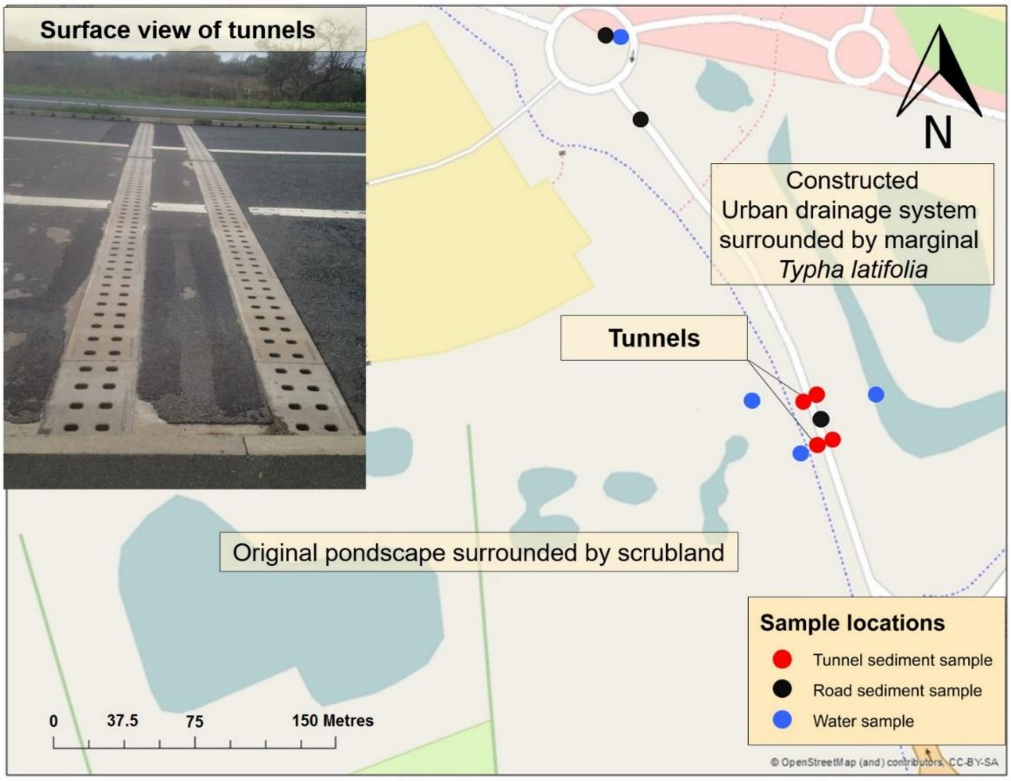

Figure 2. Comparison of major physico-chemical characteristics in sediments between tunnel and reference sites. Data aggregated from all sample months. $n$ = 24 for reference sites, $n$ = 56 for tunnel sites.

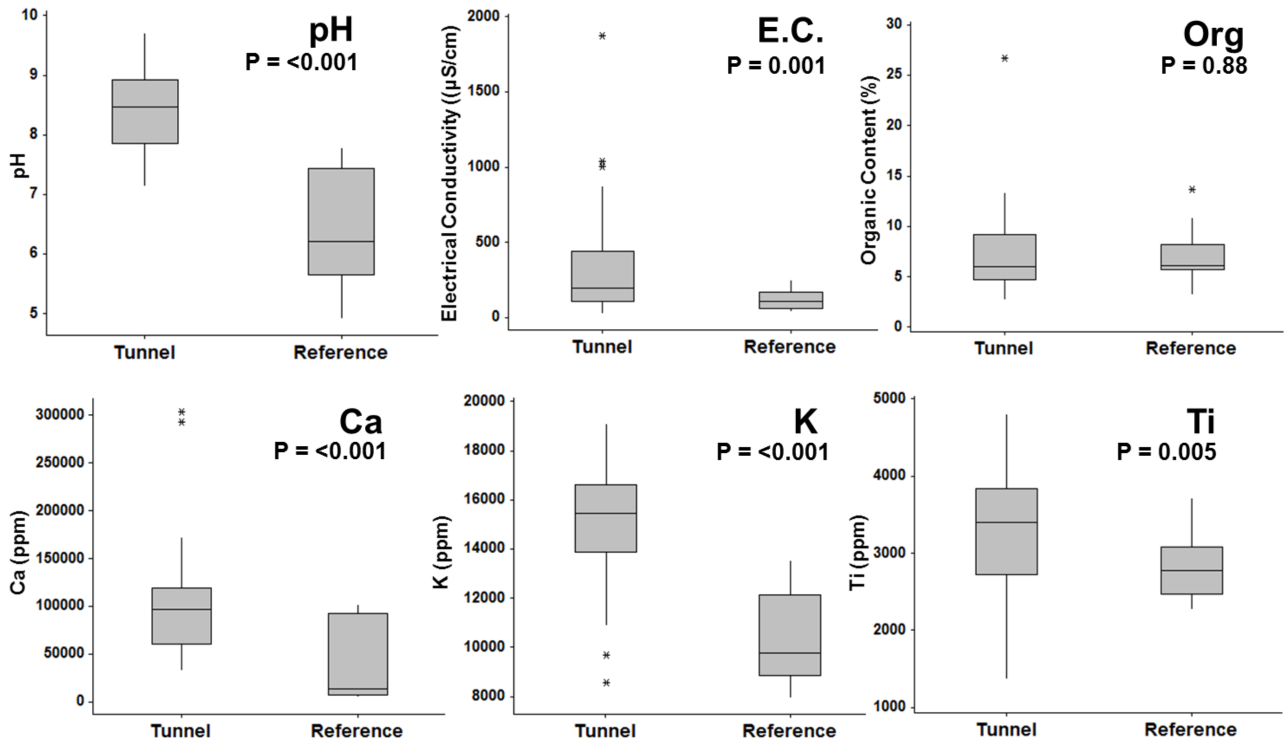

Figure 3. Comparison of sediment electrical conductivity in tunnels between autumn and spring sampling. $n$ = 18 for both autumn and spring.

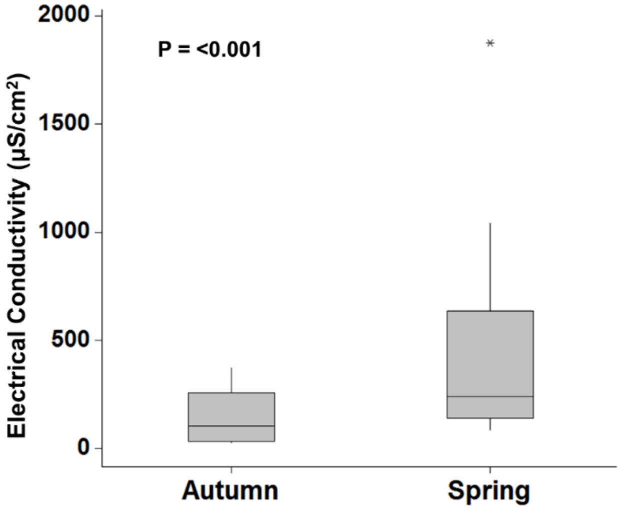

Figure 4. Comparison of major and minor elemental composition of sediments between tunnel and reference sites. Data aggregated from all sample months. $n$ = 24 for reference sites, $n$ = 56 for tunnel sites. Green line shows Threshold Effects Level; Red line shows Probable Effects Level (see text for description)

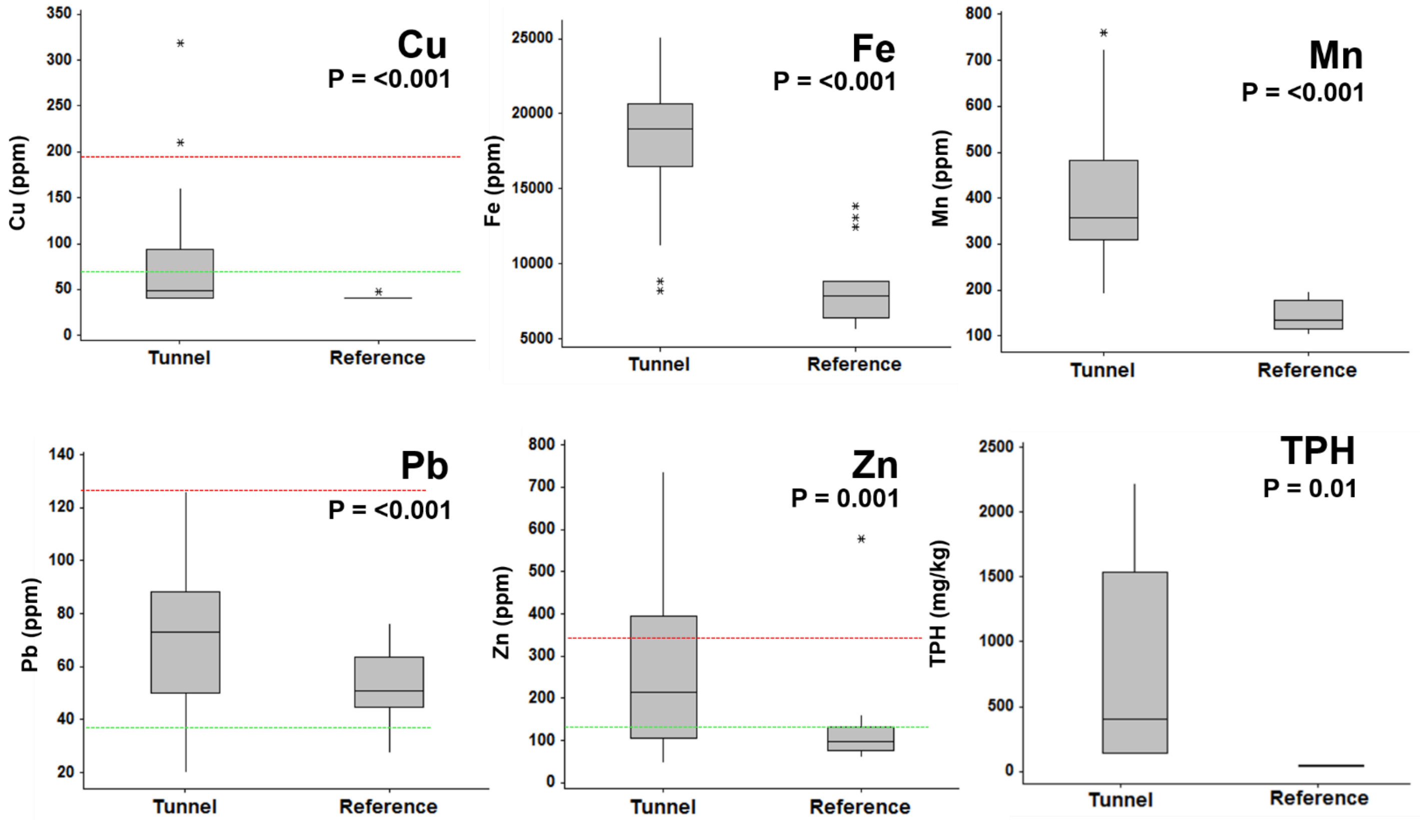

Table 1: Range of filtered elemental concentrations in water samples. *All elements in μg/L excluding Ca, Mg, K and Na which are displayed in mg/L. *n* = 3 for Sustainable Urban Drainage System (SUDS) and Tunnel mouth. Ponded road surface samples were only available for collection on one occasion (Jan 16).

| | SUDS | Tunnel entrances | Road Surface |
|---|---|---|---|
| **pH** | 7.1-8.7 | 9.6-11.4 | 8.2 |
| **E.C. (μS/cm)** | 507-1832 | 710-3471 | 10,200 |
| **Ca** | 58-116 | 132-311 | 30 |
| **Mg** | 30-85 | 21.4 | 20 |
| **Na** | 30-290 | 488-646 | 1190 |
| **K** | 4-9 | 5-13 | 4 |
| **Al** | 31-96 | 201-253 | 105 |
| **Cr** | 1-2 | 9-12 | 1 |
| **Cu** | 5-11 | 4-6 | 38 |
| **Fe** | 22-2585 | 10-16 | 33 |
| **Mn** | 12-120 | 6-7 | 30 |
| **Pb** | <LOD | <LOD | <LOD |
| **Se** | 7-19 | 6-41 | 16 |
| **Sr** | 270-358 | 280-474 | 128 |
| **Zn** | 5.8-5.8 | 1-2 | 10 |
| $SI_{CaCO3}$ | -1.14 to +0.63 | +1.45 to +1.97 | -1.28 to -1.45 |

Table 2. Range of values for physicochemical parameters of sediment and elemental concentrations (ppm) taken for different sediment samples.

| | **Reference** | **Tunnels** | **Road** |
|---|---|---|---|
| **pH** | 4.9-7.8 | 7.3-9.6 | 7.1-9.7 |
| **E.C. (µS/cm)** | 40.7-249.6 | 44.9-1872 | 26.9-874.1 |
| **Ca** | 4819-101868 | 32400-172800 | 30300-88861 |
| **Fe** | 5602-13846 | 11194-23502 | 8157-24184 |
| **K** | 7941-13538 | 12388-19089 | 8561-13538 |
| **Ti** | 2277-3710 | 2550-4806 | 1363-4520 |
| **Cu** | 40-47 | 40-210 | 75-320 |
| **Mn** | 65-196 | 191-761 | 210-725 |
| **Pb** | 27-76 | 20-126 | 24-76 |
| **Zn** | 61-279 | 48-736 | 65-491 |