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DIFFUSION TUBES: LOW-TECH BUT USEFUL

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Presented at the
36th CRC Real World Emissions Workshop
San Diego, California

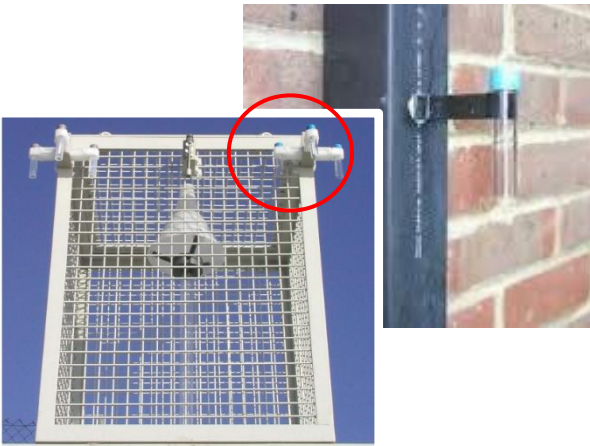
March 8-11, 2026

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Nitrogen Dioxide (NO₂) Diffusion Tubes



Diffusion Tubes amongst the oldest and most widely used Environmental Monitoring tools:

- NO₂ tubes use a chemical absorbent, usually triethanolamine
- Sample air by ambient diffusion
- Typically provide 4-week to 1-month average measurements

Pros

Easy to Deploy
Low-Cost
Known Commodity

*No in-use power and minimal infrastructure and permissions;
Few £s(\$s)/tube, so widely used in larger/longer-scale studies;
Well established method*

Cons

Labour-Intensive
Delayed Reporting
Indicative Method
(Time Resolution?)

*Manual deployment/collection;
Offline analysis and bias correction;
Less accurate/precise than continuous analyser, often $\pm 15-25\%$ but more recently $\pm 12-15\%$, BUT still NOT strictly evidentiary*

References: (1) Local Air Quality Management - Technical Guidance (TG16), April 2016. Defra and the Devolved Administrations [\[source\]](#); (2) Pfeffer, U., Zang, T., Rumpf, E.M., Zang, S., 2010. Calibration of diffusive samplers for nitrogen dioxide using the reference method—Evaluation of measurement uncertainty, Gefahrstoffe, Reinhaltung der Luft, 11(12), pp.500-506 [\[source\]](#); (3) European Union Directive 20/50/EC - on Ambient Air Quality and Cleaner Air for Europe, Official Journal of the European Union, L 152/1 - 44, June 2008 [\[source\]](#).

Case Study: the Bradford Clean Air Zone (CAZ)

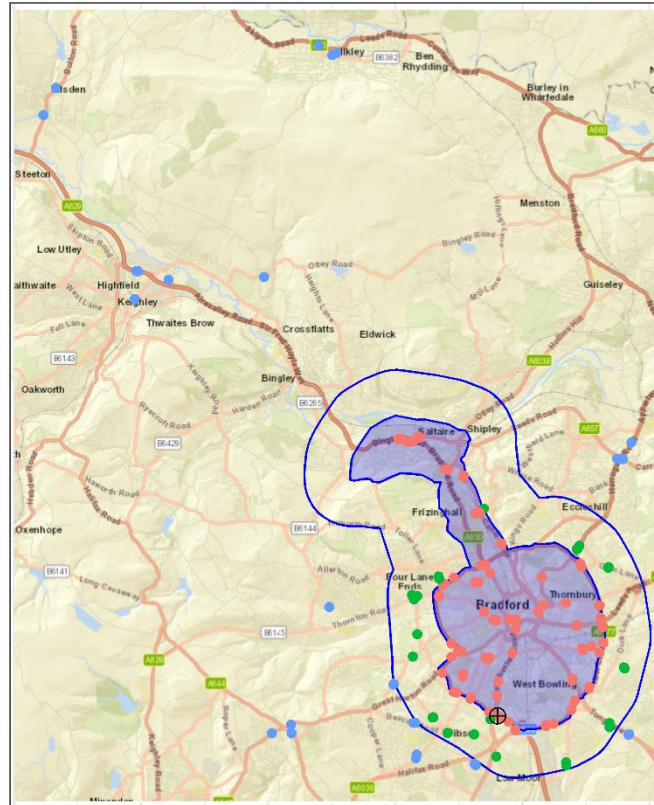
UK Metropolitan Borough, City of Bradford and nearby towns (pop 0.56m, 9th largest), culturally diverse, disadvantaged (ca. 41% mainly urban core amongst most deprived in UK), but subject to efforts to 're-level'

Bradford

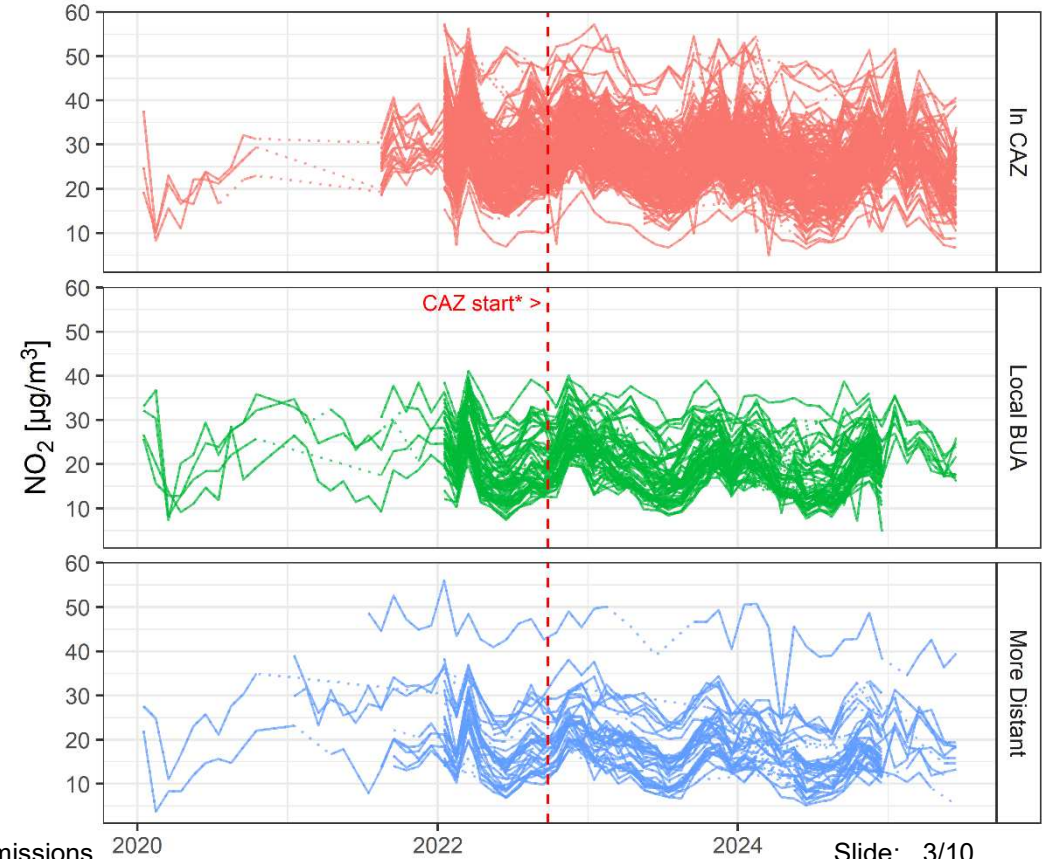
Dataset

10,408 samples
 148 sites
 67% in CAZ;
 21% in the local built-up area (BUA)
 12% more distant locations
 At 64 Intervals
 2020 to mid-2025
 BUT focusing on 2022-2024
 (high coverage period)

(All map layers: (c) OpenStreetMap/ESRI contributors)



Bradford DT Data (bias corrected)





Difference-in-Differences (DiD)

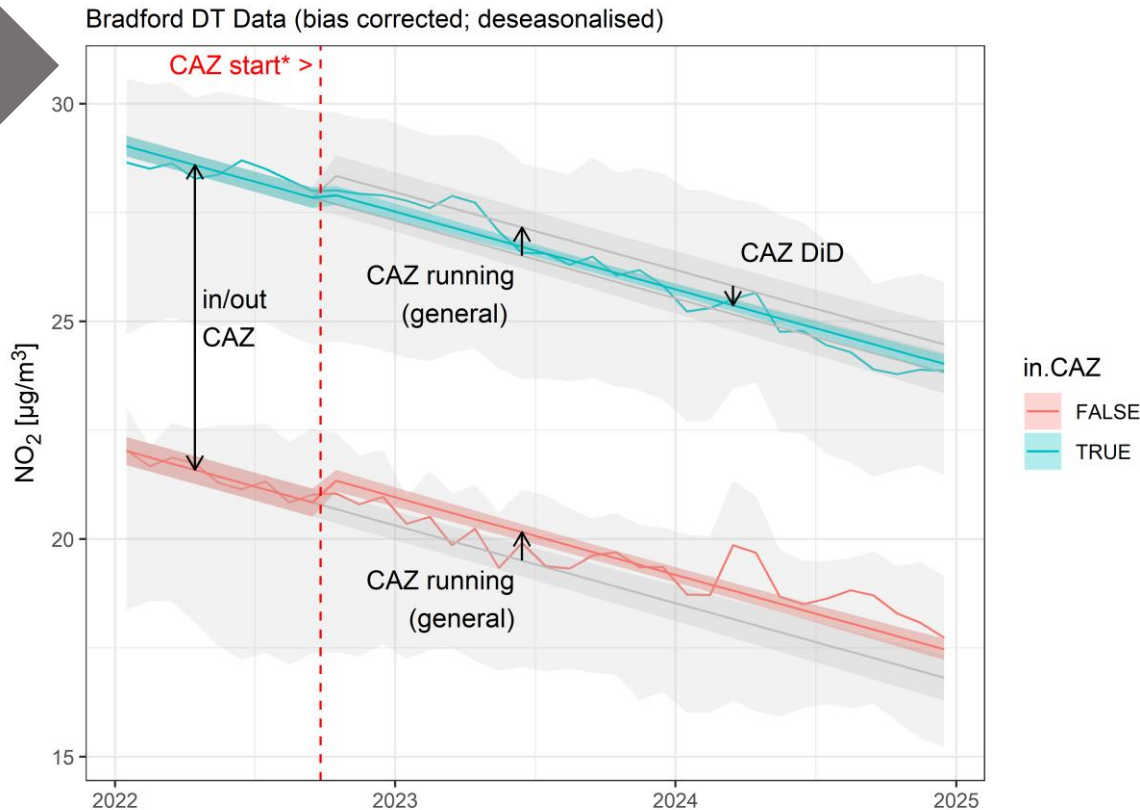
A 'treatment' and 'control' model that attempts to estimate the causal effect of an intervention by comparing changes over time in similar but not explicitly identical groups

preprocessing, deseasonalise: $[NO_2]_{ds} = [NO_2] - f(\text{day-of-year})$

Model \rightarrow $[NO_2]_{ds} = f(\text{date}) + \boxed{[CAZ.\text{running}] + [in.CAZ]}$ + $\boxed{[DiD]}$

Dummy Variables: yes=1/no=0 Interactive Term: CAZ.running \times in.CAZ

Output \rightarrow



Predicted NO_2 Trends:

- A pre-CAZ decrease of ca. $0.005 \mu\text{g}/\text{m}^3/\text{day}$ (ca. $1.5 \mu\text{g}/\text{m}^3/\text{year}$)
- Levels inside the CAZ of ca. $7.0 \mu\text{g}/\text{m}^3$ higher than those outside the CAZ
- After the CAZ started, decreases were not as rapid and by end-of-2024 levels were on average $0.65 \mu\text{g}/\text{m}^3$ higher than expected pre-CAZ
- (This is general in AND out CAZ, and could just mean the rate of regional improvement was slowing)
- BUT in the CAZ by comparison to outside the CAZ NO_2 levels were ca. $0.45 \mu\text{g}/\text{m}^3$ better

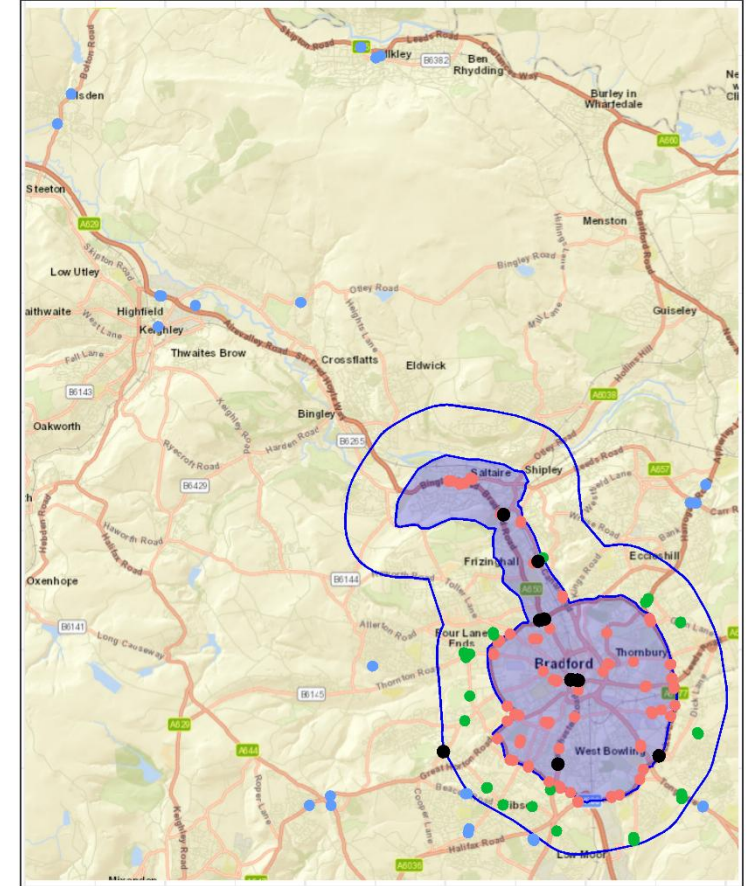
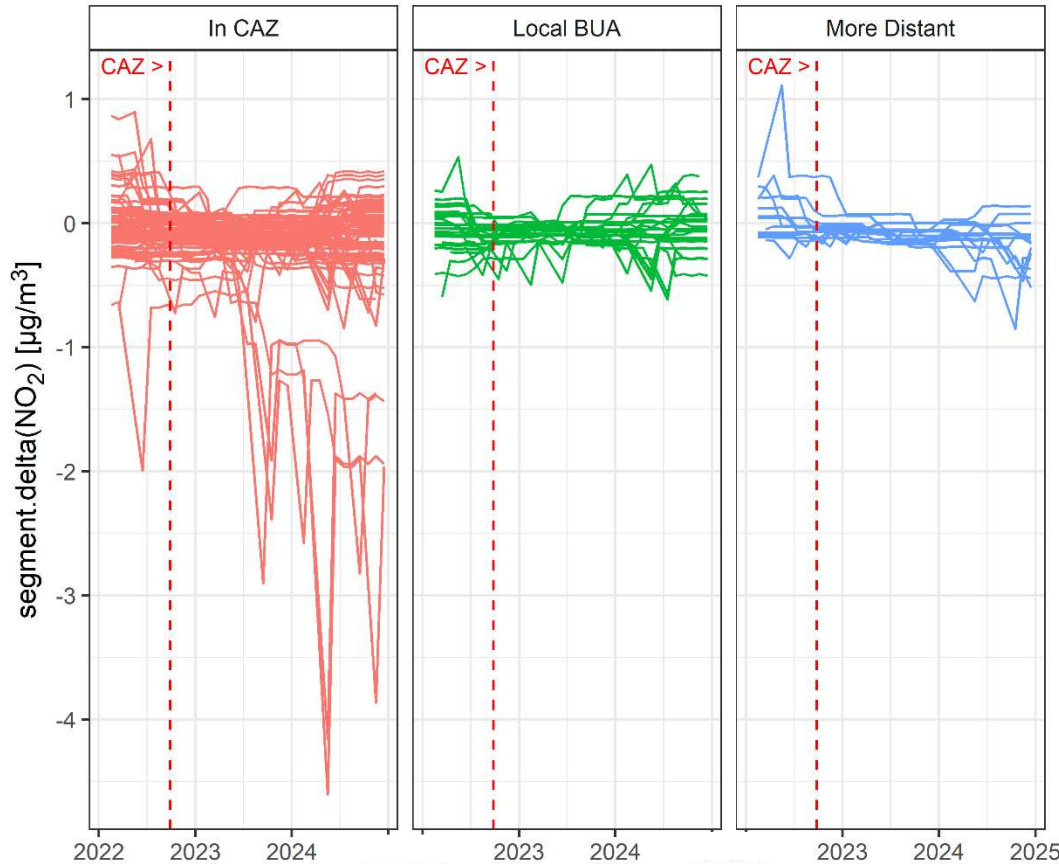
Supporting Evidence: Break-Points/Segments (BP/S)

A 'rolling window' strategy that looks for points in a time-series where conditions change

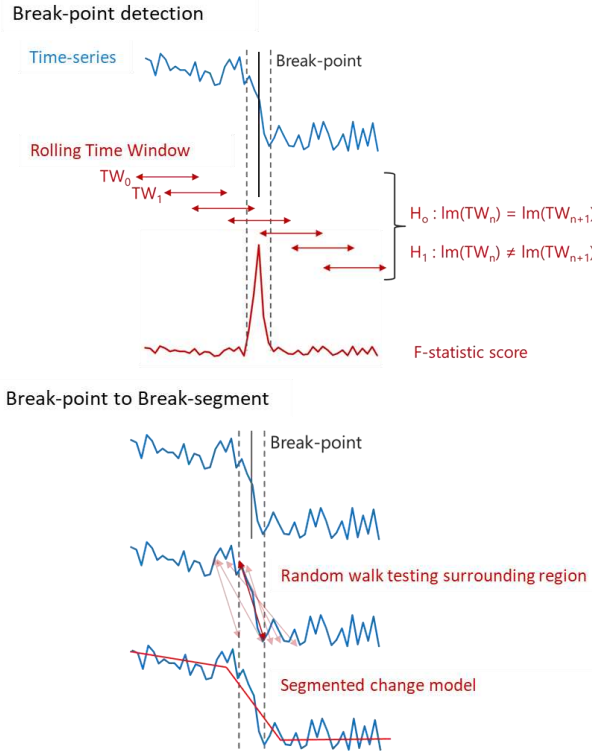
Method → BP/S([NO₂]_{ds})
3-month time windows

By-location testing shows large and persistent decreases BUT only at some sites, and more often starting 2023-2024...

Bradford DT Data (bias corrected; deseasonalised)



... and the 'black sites' above are where we see most of these larger improvements





Supporting Evidence: Cluster Analysis

Grouping of samples based on time profile similarities

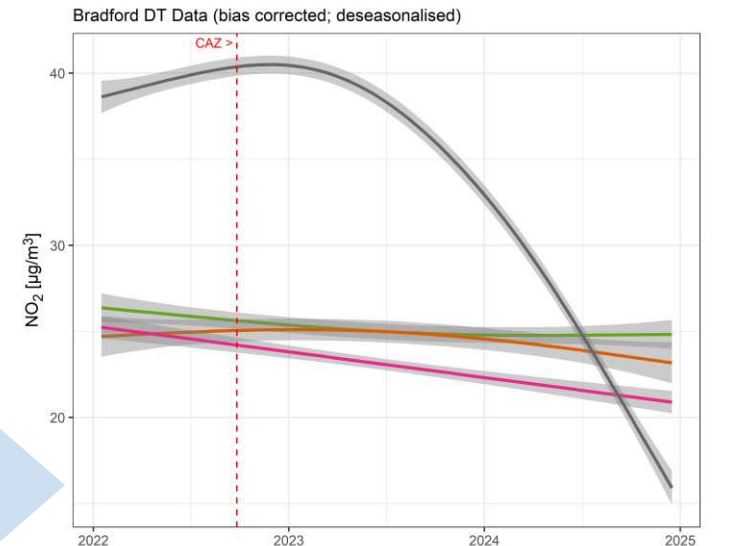
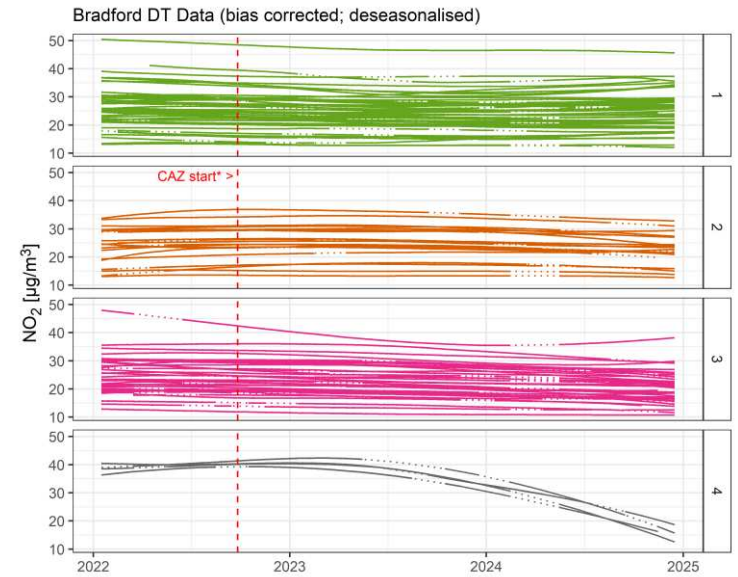
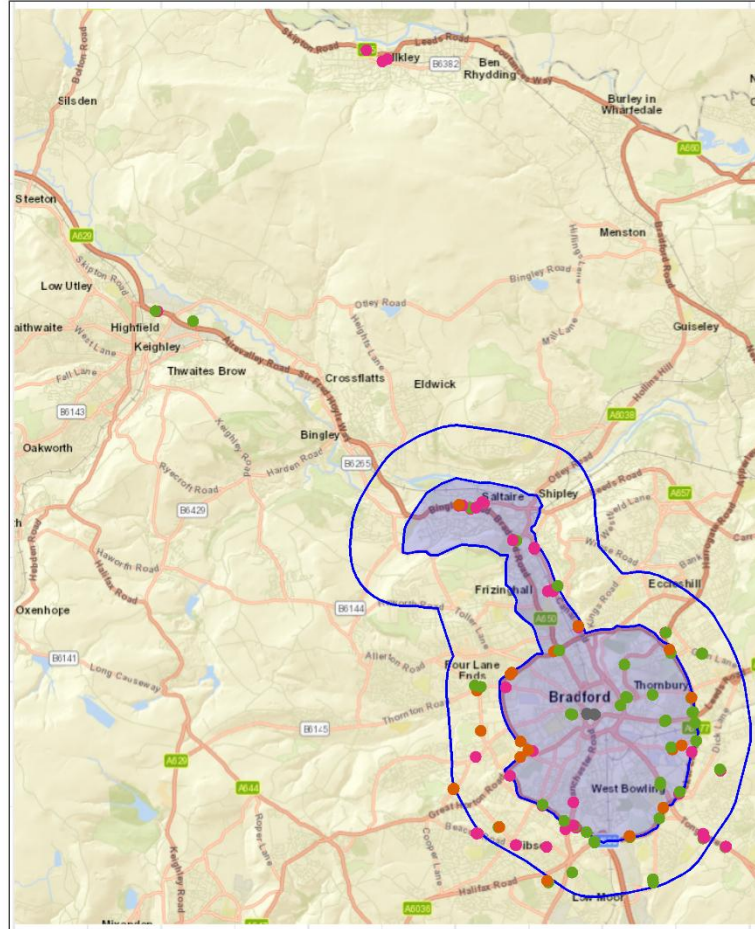
Step 1 Normalising $[NO_2]_{ds}$

$$\mu_i = [NO_2]_{ds} / \overline{[NO_2]_{ds}}$$

Step 2 Silhouette test to determine number of clusters

Step 3 Cluster, using the 'clara' model for large datasets

$$y_i = \sum_{cl=1}^{CL} \sum_{z=1}^Z S_{cl(0,1)}(\mu_{i,cl}) + e_i$$



Indicates large benefits at the CAZ centre, different behaviour split roughly to west and east, BUT also notable heterogeneity



Regional Model (1); Build

Using ambient data, $[\text{NO}_2]$, because aim here is to apportion contributions...

Step 1

$$[\text{NO}_2] = f(\text{date}) + f(\text{day-of-year}) + [\text{CAZ.running}] + [\text{in.CAZ}] + [\text{DiD}]$$

(DiD MODEL)

Adding seasonal term $f(\text{day-of-year})$ to Model

Step 2

Extract response functions for date and day-of-year from DiD MODEL

(BACKGROUND)

Step 3

Build Main Model allowing for limited nonlinearity (applying by location)

$$[\text{NO}_2] = \text{spline}(\text{BACKGROUND}) + \text{spline}(\text{IMPACT})$$

(MAIN MODEL)

$$\text{where IMPACT} = \begin{cases} 0 & \text{before CAZ starts,} \\ \text{date} - \text{CAZ start date} & \text{afterwards} \end{cases}$$

Step 4

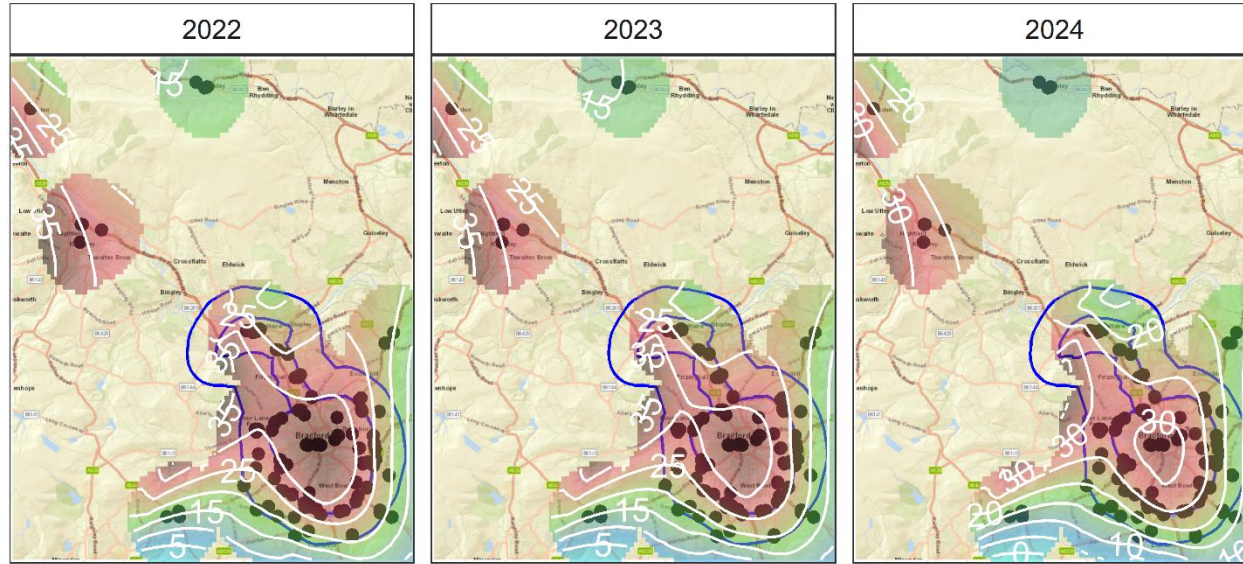
Extract BACKGROUND and IMPACT response functions from MAIN MODEL
Fit surfaces as generalised (and smoothed/conservative) descriptors

(OUTPUTS)

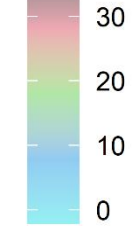
Regional Model (2); Results



Background

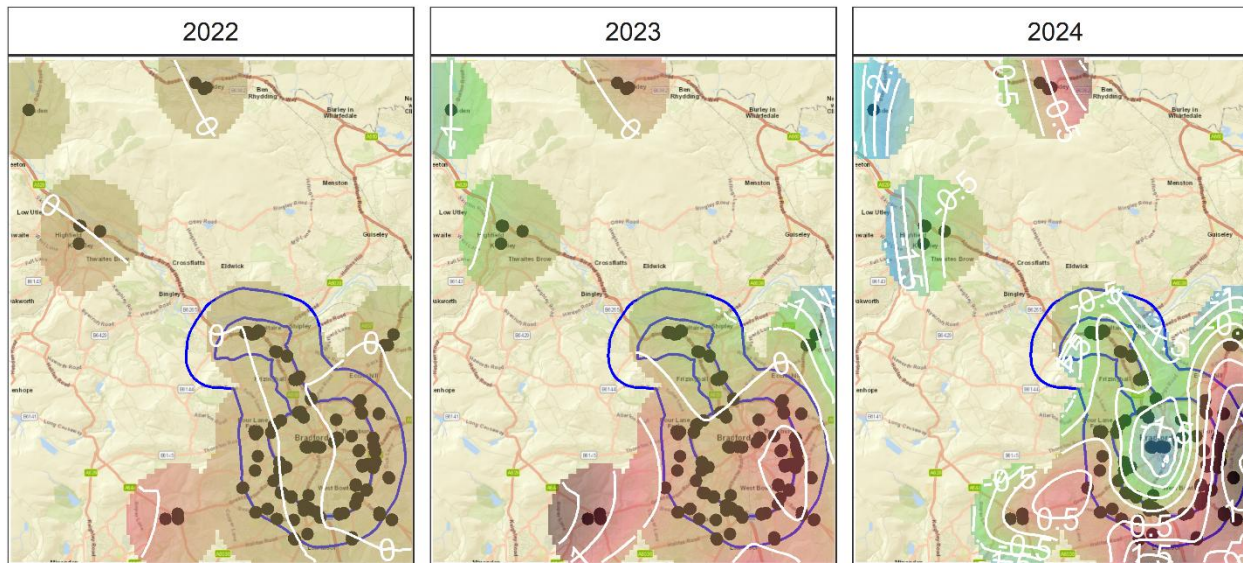


background

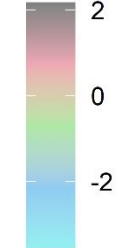


*Background NO₂ Trends:
Seen across region
ca. 1.5 µg/m³/year
(like DiD Prediction)*

CAZ Impact



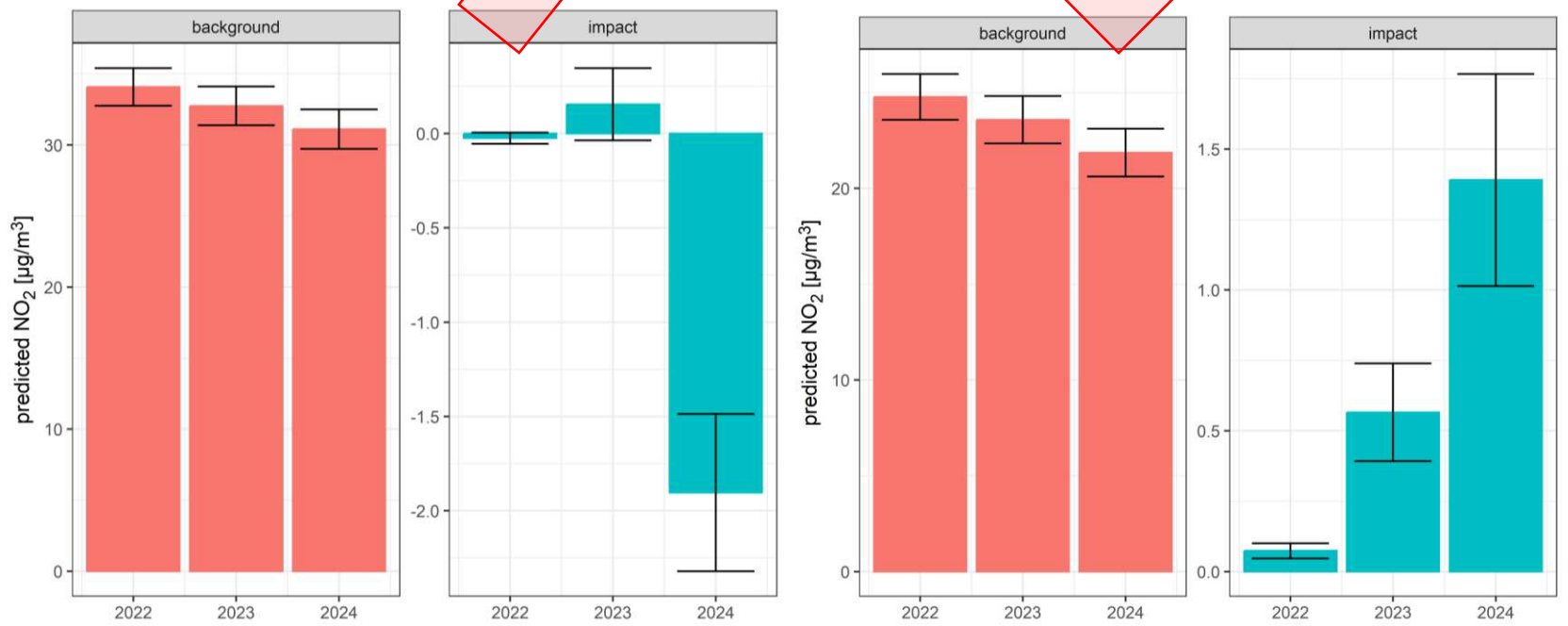
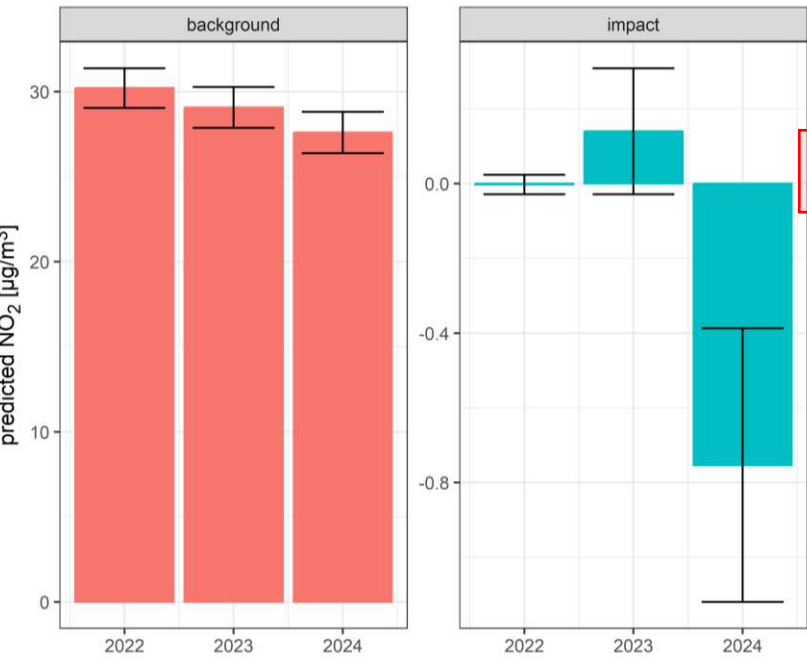
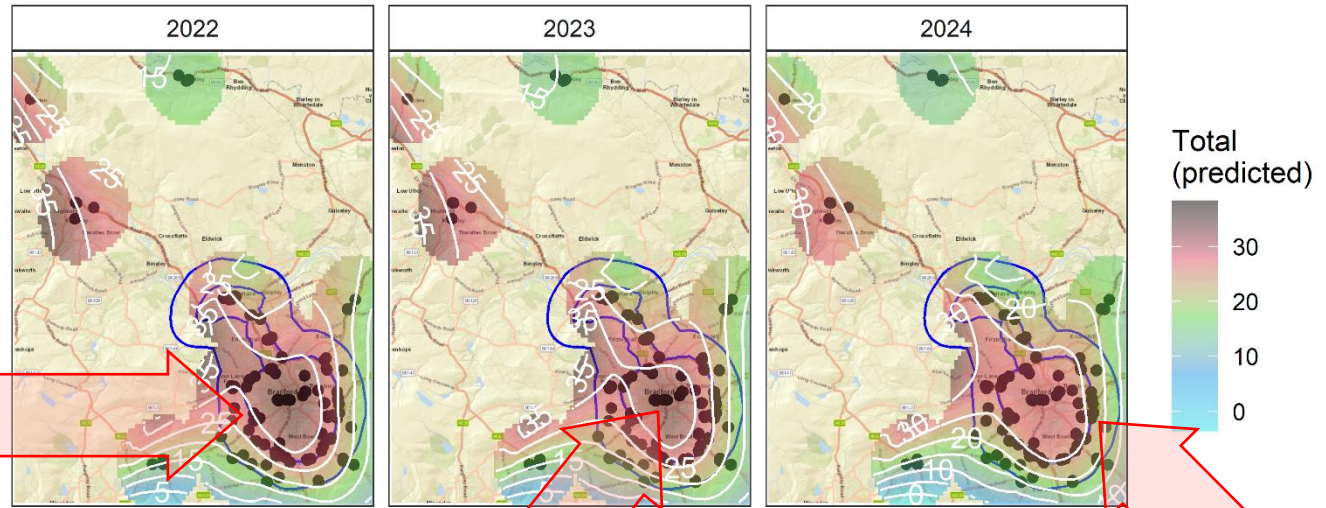
impact



*CAZ Impact NO₂ Trends:
Much more
heterogeneous*



Regional Model (3); Selected Results





Conclusions and Comments

Key Findings:

- NO₂ Improvements in Bradford in recent years are likely due to combination of regional/background and CAZ-related contributions
- The regional/background contribution is estimated at -1.5 µg/m³/year
- The CAZ-related contribution is much more heterogeneous, may have been delayed, and is conservatively estimated to range from -1.9 µg/m³ in the CAZ to 1.3 µg/m³ at its eastern boundary and in the surrounding area; consistent with a combination of improvements and dirty-vehicle displacement from the city centre into the surrounding area

Outputs:

- Software developed as part of this work
- (<https://github.com/karlorpkins/DTEval>)

Funding: (and caveats)

- Defra/IPSOS Mori - NO₂ Evaluation Phase 2
- The views and opinions expressed herein by the authors are their own and do not necessarily reflect those of UK Government or any agency thereof