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Highway deicing salt dynamic runoff to surface water and subsequent infiltration to groundwater during severe UK winters

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Abstract

Dynamic impact to the water environment of deicing salt application at a major highway (motorway) interchange in the UK is quantitatively evaluated for two recent severe UK winters. The contaminant transport pathway studied allowed controls on dynamic highway runoff and storm-sewer discharge to a receiving stream and its subsequent leakage to an underlying sandstone aquifer, including possible contribution to long-term chloride increases in supply wells, to be evaluated. Logged stream electrical-conductivity (EC) to estimate chloride concentrations, stream flow, climate and motorway salt application data were used to assess salt fate. Stream loading was responsive to salt applications and climate variability influencing salt release. Chloride (via EC) was predicted to exceed the stream Environmental Quality Standard (250 mg/l) for 33% and 18% of the two winters. Maximum stream concentrations (3500 mg/l, 15% sea water salinity) were ascribed to salt-induced melting and drainage of highway snowfall without dilution from, still frozen, catchment water. Salt persistance on the highway under dry-cold conditions was inferred from stream observations of delayed salt removal . Streambed and stream-loss data demonstrated chloride infiltration could occur to the underlying aquifer with mild and severe winter stream leakage estimated to account for 21 to 54% respectively of the 70 t of increased chloride (over baseline) annually abstracted by supply wells. Deicing salt infiltration lateral to the highway alongside other urban/natural sources were inferred to contribute the shortfall. Challenges in quantifying chloride mass/fluxes (flow gauge accuracy at high flows, salt loading from other roads, weaker chloride-EC correlation at low concentrations), may be largely overcome by modest investment in enhanced data acquisition or minor approach modification. The increased understanding of deicing salt dynamic loading to the water environment obtained is relevant to improved groundwater resource management, highway salt application practice, surface-water - ecosystem management, and decision making on highway drainage to ground.

Key words: Deicing salt, Chloride, Highway, Urban, Groundwater, Surface water, Winter

1. Introduction

Application of highway deicing agents, most commonly sodium chloride salt, is vital to road safety. Most applied salt, however, is ultimately expected to enter the water environment. The legacy of deicing salt gradually accumulating in aquifers is of concern across cold-climate regions (Bester et al., 2006; Foos, 2003; Gedlinske, 2013; Godwin et al., 2003; Harte and Trowbridge, 2010; Howard and Maier, 2007; Kelly, 2008; Lundmark and Jansson, 2008; Meriano et al., 2009; Nystén 1998; Thunqvist 2004; Perera et al., 2013; Viklander et al., 2003; Warner and Ayotte, 2014; Williams et al., 1999). Salt application in more temperate areas, although experiencing less snowfall, may still be significant. The Midlands region of the UK studied herein has fairly limited snowfall, yet may often face near-freezing damp or icy conditions that warrant salt application (Andersson and Chapman, 2011). Indeed, such conditions, amongst other factors including the mode of salting and legal requirements to keep roads free of ice and snow, result in the UK having relatively high salt spreading rates compared to similar cold-climate countries (Booth et al., 2011).

Salt application trends over recent decades may remain influential. This is particularly true where aquifers have high storage capacity and correspondingly low turnover of resource. In the US, for example, salt use has increased threefold since the 1970s in the area overlying the Northern glacial aquifer that supplies one-sixth of the nation's population (Nixon, 2013; Warner and Ayotte, 2014). In the UK, significant salt use was triggered by the severe 1962-63 winter with around 1 Mt (million tonnes) of salt being applied that year (Thornes, J.E., *pers. commun.*). Hitherto Thornes indicates grit from power stations had been rather ineffectively used. The 1980 Highways Act was also instrumental in conferring a duty of care on highway authorities to clear snow and ice. This resulted in a step-change in UK operations and the development of a national ice prediction system in the mid 1980s that served as a forerunner to modern route-based forecasting and maintenance decision support systems (Chapman and Thornes, 2006; Handa et al., 2006; Thornes and Chapman, 2008; Nixon, 2013).

Currently, the UK has over 400,000 km of main roads of which 30 % are salted via 3500 salting routes (Thornes and Chapman, 2008). The UK applies around < 1 Mt of salt during a mild winter, 1 - 2 Mt for an average winter and 2 - 3 Mt in a severe winter (Thornes, J.E., *pers. commun.*). This compares to 10 to 20 Mt in the US and 5 Mt in Canada (Environment Canada, 2004). Climate change may additionally influence future applications. Andersson and Chapman (2011) predict declining salt application for the UK (West) Midlands and model 'frost days' in the region to decline from the present 69 to 28 days by 2080. Somewhat contrary to this longer term expectation, our winter field campaigns were conducted during two of the UK's most severe recent winters of recent decades. Public and press interest was notable during 2009-10 as deicing salt supplies dwindled and concerns were expressed over the fate of the vast quantities of salt, indeed record levels, being applied (Hickman, 2010).

Estimating the proportion of salt accumulating in groundwater is challenging. In Toronto, where Howard and Maier (2007) indicate deicing salt has become a potential constraint on urban growth, Perera et al. (2013) estimate that 60% of Toronto's applied road salt drains to surface water and leaves the catchment. The corresponding 40% balance infiltrates to the aquifer. Decreases in baseflow chloride discharges now result in a net aquifer accumulation of 19% of the annual Toronto salt application. In Sweden, Blomqvist and Johansson (1999) estimated 20 to 63% of applied deicing salt was transported by air and deposited on adjacent ground 2 to 40 m from the highway reaching a maximum of 100 m with over 90% deposited within 20 m. Higher percentages were ascribed to greater snowfall, more splash generation and ploughed snow displacement and have been modelled using approaches developed by Lundmark and Jansson (2008). Deposited salt lateral to the highway is likely to infiltrate to groundwater.

Our interest is to investigate the potential for salt infiltration through a leaky streambed that may constitute a significant line-source to the underlying aquifer. This scenario is particularly important where well fields have contributed to an influent stream condition and subsequently prove to be a receptor of the stream contamination present. Our goal was to quantitatively evaluate the impact of winter deicing salt applications at a major highway ('motorway') interchange on the surrounding water environment; in particular, a surface-water reach that receives storm-water discharges from the highway, but leaks to groundwater and may be partly responsible for gradually rising chloride observed in nearby public water supply (PWS) wells (EA, 2010).

Objectives set were: to understand factors controlling winter season dynamic stream water-quality and the transients of storm-sewer discharges of motorway runoff; to prove surface-water – groundwater connectivity and estimate deicing salt infiltration to the underlying aquifer; and, to consider the potential for the 'pollutant linkage' studied (salt application - highway runoff – storm-sewer discharge – stream transport and infiltration - groundwater advection and abstraction) to account for rising chloride in the supply wells.

Assessing such pollutant linkages, expected to fully develop over years to decades at relevant cross-disciplinary field-scales, is rarely attempted. It is, however, fundamental to assessing the long-term impact of both historic and future deicing activity and integral to the holistic surface-water – groundwater – landuse management agenda of the EU Water Framework Directive.

2. Study area setting

2.1. Site scenario

The sstudy located at the Worcestershire – West Midlands border was motivated by Environment Agency interest to better understand gradually rising chloride in PWS wells located close to the national motorway network. Specifically, there was interest to understand the possible influence on the wells of a nearby stream, the Battlefield Brook, that received storm-sewer discharges of motorway runoff (Environment Agency (EA), 2010). The 44 km^2 area Bromsgrove West Groundwater Management Unit is part of the Permo-

Triassic Sandstone aquifer, the UK's second most important aquifer (Allen et al., 1997; Tyler-Whittle et al., 2002). This Unit contains seven PWS wells licensed to abstract 73 Ml/d (mega-litres per day) (EA, 2010). Actual abstraction has been less amounting to 26 Ml/d in 1965 to a maximum of 44 Ml/d in 1991 falling to 35 Ml/d in 2007 (EA, 2010).

Our focus is on two PWS wells within the Bromsgrove Formation that are situated relatively close to both the motorway network and Battlefield Brook (Fig. 1). The southernmost well, established in 1903, and the other in 1955 are together licensed to abstract 23 Ml/d. Chloride concentrations in the southern well steadily rose from around 25 mg/l in 1974 to stabilise at around 45 mg/l by 1992 followed by a marginal decline over the 2000s (EA, 2010). Data suggest a moderately stable steady-state interaction with surrounding sources. The northern well has exhibited a prolonged increase from around 15 mg/l in 1974 to 35 mg/l and was still increasing in 2008 (EA, 2010). Abstracted concentrations though remain far below the 250 mg/l drinking water standard (DWS) with increases in both wells amounting to around 20 mg/l chloride. Their combined actual abstraction of around 10 Ml/d causes this increase to amount to some 70 tonnes per annum (t/y) of additional chloride being abstracted from the aquifer compared to that historically abstracted in 1974. These concentrations compare to background chloride of <10 to 20 mg/l observed over 1975-85 in the five PWS wells located more remote from highway influence (EA, 2010).

2.2. Catchment - highway drainage

The Battlefield Brook is known to leak in the study area (EA, 2010) and thus has potential to serve as a line-source to the underlying aquifer. It receives storm-sewer discharges at three locations conveying drainage from 7 km of 'motorway' at the M5 - M42 interchange on the south-west hub of the national motorway network encircling the UK's second largest city, Birmingham (Fig. 1). Motorways typically have 3 lanes or more in each direction (Fig. 2). The M5 section was constructed in 1960 – 63 and widened in 1979. The M42 was opened in the late 1980s.

The catchment was monitored to just downstream of the M5 – M42 interchange and southern supply well (Fig. 1). The stream is 5.5 km from its source at this point and has a catchment area of 12.8 km^2. The stream rises from perched-groundwater rural springs in the vicinity of the steep slopes of the Lickey Hills that comprise the Permian Clent Formation – a volcanic breccia in a mudstone matrix (EA, 2010; Gamble, 2013). The hills form part of England's national divide with catchment drainage southwards towards the River Severn. Birmingham, on the opposing side of the divide, drains to the River Tame and North Sea and hence does not influence the study area (Rivett et al., 2011). The motorway crosses and topographically drains to the stream where storm-sewer discharges occur at three locations (Fig. 1). For convenience, we divide the study reach to sub-reaches A to C indicated in Fig. 1 at these crossing points. Several A- and B-roads and some minor C-roads also drain to the stream.

2.3. Groundwater vulnerability and surface-water interaction

The study PWS wells have total catchment and outer source (well) protection zones that extend under the Battlefield Brook and motorway (Fig. 1). The aquifer is vulnerable due to its limited protection by sparse alluvial and glacial superficial deposits. The M5 motorway passes through cuttings in the sandstone where any runoff not collected by engineered storm-water drainage may directly enter the cutting face and infiltrate the aquifer (Fig. 1; see Supplementary Material Fig. S1 for a selection of study area photographs). The deeper Sherwood sandstone reaches some 400 m thickness around the southern PWS well that is completed mid-aquifer, to around 200 m depth. The more northern well at *c*. 250 m depth appears to fully penetrate the sandstones at this location possibly entering the underlying Clent formation (EA, 2010).

Kidderminster and Wildmoor Formations underlie the upstream reach and are downthrown at the Lickey Fault; the brook downstream is underlain by the Bromsgrove sandstone Formation (Fig. 1). The Kidderminster comprises sandy conglomerates and sandstones and transitions to the Wildmoor that comprises a series of sandstone beds separated by thin laterally extensive mudstone beds. The Bromsgrove overlies the Wildmoor and comprises conglomerates, sandstones and mudstones (EA, 2010; Tyler-Whittle et al., 2002). Although vulnerable, the large aquifer thickness and storage capacity offer significant dilution potential. Hydraulic conductivity values are around 0.5 – 2.5 m/d and matrix porosity around 25 % with some fracturing present (EA, 2010). The hydraulic gradient is from north-east to south-west, consistent with topography and stream flow direction (EA, 2010). The Lickey Fault somewhat impedes southwards groundwater flow with reduced gradients south of the fault. This is consistent with the southern PWS well sourcing groundwater from a relatively large area (Fig. 1).

Aquifer abstraction has lead to a depressed water table and to the groundwater - Battlefield Brook relationship coming under scrutiny (EA, 2010). Headwaters comprise a reliable flow of 0.3-1.2 Ml/d from springs in the adjacent formation (Gamble, 2013), however, in the recent past (and longer) the stream became losing within the study area, occasionally becoming dry (EA, 2010). Licensed aquifer abstraction was hence reduced from 53 Ml/d to 39 Ml/d close to the stream and 2006 saw the installation of an ‘Alleviation of Low Flow’ (ALF) borehole to augment low summer flows by up to 2 Ml/d. Summer augmentation is triggered by low flows measured on the EA stream flow gauge installed immediately upstream of the second M5 crossing point (Fig. 1), the ALF borehole discharging to the stream a little further upstream. Despite these reductions in PWS abstraction, the Bromsgrove West Unit is still considered over-abstracted and is targeted for improvement of Water Framework Directive quantitative status from poor to good by 2027 (EA, 2010).

2.4. Possible sources of salt (chloride)

Winter salt applications will have occurred to the motorways in the study area since their respective openings (Thornes, J.E., *pers. commun.*). Hence parts of the network may have contributed salt loads to the underlying aquifer for over 50 years. This is alongside potential inputs from salting of the local A/B/C-road network (A roads are major 1- or 2-lane each-way highways, B are significant 1-lane each-way roads and C are minor roads).

Other potential sources of chloride to the aquifer, besides the losing stream focused on in our study, include: the component of highway deicing salt application that has been deposited on porous ground lateral to the highway that may infiltrate to the aquifer; any leakage to ground that may occur at the highway salting depot (Fig. 1); landfills, particularly where unlined; leakage from urban sewers; septic tank etc. discharges; and, natural sources such as salinity migration from geochemically distinct parts of the subsurface - aquifer, for example, groundwater abstraction induced migration of salinity from deep or adjoining geological formations.

3. Methods

3.1. Surface-water and streambed: flow and water-quality monitoring

Paired stream and streambed monitoring sites (Sites 1 – 6) were installed immediately upstream and downstream of each motorway - stream crossing and motorway runoff storm-sewer discharge point (Fig. 1). At Site 1 the stream is <1 m wide becoming 2 - 3 m wide by Site 6 (Fig. 1; Supplementary Material Fig. S1). Relationships between surface water and streambed - groundwater were established at each site via streambed installation of an integrated drive-point piezometer - multilevel sampler (Rivett et al., 2008). Samplers comprised a central flexible HDPE tubing (10 mm ID) with a 10 cm screened interval that had two narrow diameter flexible Teflon® screened tubes (1.6 mm ID) attached at different depth increments yielding three points that could be used for water quality sampling at 0.15, 0.3 and 0.45 m below streambed. Hydraulic head was measured in the deepest point that, combined with stream stage measurement, allowed estimation of flow direction and hydraulic gradient across the streambed.

Sampling was conducted on 9 occasions during the 2009-10 and 2012-13 winters. Stream stage and streambed head measurements, streambed water quality samples from 3 depths and a surface-water quality sample were obtained from each site via peristaltic pump or syringe suction purging and sampling. Due to the shortness of the winter working day (7 hours) and the difficulty of pumping some monitoring points, complete sample sets were not always feasible (sampling spread over 2 days was avoided due to the system transients). Run-off from the motorway was sampled on 2 visits from an open drain discharging immediately upstream of Site 4 (Fig. 1; Supplementary Material Fig. S1). Cold-stored samples were submitted (same day) to Environment Agency laboratories with analysis undertaken for a suite of 30 analytes including all major and minor anions/cations, toxic metals (0.45 μm filtered on site) and TOC (total organic carbon). We primarily present electrical conductivity (EC) and chloride data herein alongside some major ion data. Chloride is expected to behave conservatively in the subsurface sandstone environment (unlike sodium that may be subject to ion exchange). Over 99.9% of the TDS (total dissolved solids) mass measured in the Battlefield Brook surface-water samples was attributed to the major ions. The ion mass balance on these samples was just over 2% with typical analytical error on the chloride analysis being around 3%.

3.1.1. Continuous temporal monitoring

A *Diver*^{TM} logger was installed at Site 6 in 2009-10 to monitor temporal stream-water quality at the most downstream point of the study area. Readings of pressure (allowing conversion to river stage), temperature and EC (as a surrogate for chloride) were recorded at 10 minute intervals. A continuous record of stream flow data was also obtained from the flume stream gauge immediately upstream of Site 3. The gauge was installed to monitor low flows and establish the need for augmentation of streamflow in the summer. For this reason measurement of higher flows (7.5 Ml/d) are regarded as indicative (Gamble, 2013), but appear not entirely unreasonable based on profile shape and flows monitored in a gauge downstream of the study area. High-flow data are nevertheless used with caution and acknowledged to cause uncertainties in the flow-dependent chloride mass (flux) estimates made later. Due to the complexity of the catchment upstream of Site 6 that included multiple motorway and A-, B- and C-road discharges to the steam, the 2012-13 study focused on the sub-catchment upstream of Site 3. A *Diver*^{TM} logger was deployed at the Site 3 gauged flume that allowed more reliable estimation of chloride mass flux in the stream.

Conversion of EC to chloride concentration was based upon developing chloride – EC relationships from study water samples for which both chloride concentration and EC data were available (Fig.3). Conversion of EC to chloride (mg/l) was via the following plotted relationship for EC > 400 µS/cm:

$$[Cl] = 0.3311\ EC - 118.15 \qquad (R^2 = 0.9907) \qquad \text{Eq. (1)}$$

The relationship shown in Fig. 3 is comparable to trend-lines found in studies elsewhere (Harte and Trowbridge, 2010; Howard and Haynes, 1993). Alternative fits to the data including the retention of an outlier or fitting more restricted concentration ranges by removal of the highest EC values lead to small differences (< 5%) in metrics such as the Site 3 cumulative annual chloride mass discharge.

At lower concentrations, however, other background major ions, mostly calcium and bicarbonate, become more significant (Supp. Mat., Fig. S2) and hence EC increases more rapidly for a given change in chloride. The following linear fit relationship provided an improved (compared to Eq. 1) and reasonable estimate of chloride (mg/l) for EC < 472 µS/cm (Fig. 3):

$$[Cl] = 0.0544\ EC + 12.21 \qquad (R^2 = 0.65) \qquad \text{Eq. (2)}$$

Greater variability at low EC is attributed to the decreased chloride proportion within the calculated TDS (Fig. S2). It is recognised that increased scrutiny of different component water inputs to the stream of varying major ion composition is required to improve chloride predictability at low EC. Studies elsewhere experience similar challenges. Inter-study comparisons of correlations is unlikely to be that worthwhile; in that at low EC, chloride proportions will depend on the local major ion compositions that will vary between study localities. Sensitivity analysis indicated, the Site 3 cumulative annual chloride mass discharge metric was influenced by < 3 % for various low concentrations fits trialed and altering the transition point between Eq. (1) and Eq. (2) calibrations. Still, the Eq. 2 correlation is only moderate and hence low-concentration chloride estimates are presently regarded as indicative.

Climate data (daily precipitation, hourly temperature) were obtained from the Environment Agency Frankley 3167_RK climate station (NGR SP 0072 8015) located at a comparable elevation to the study catchment about 4 Km to the north east of the Fig. 1 catchment. It is expected to be representative of the study catchment except for occasional instances of local precipitation anomalies.

3.1.2. Summer field campaigns

Summer 2010 and 2013 field campaigns were conducted to obtain visual confirmation of road drainage and connectivity of storm-sewer discharges from A/B/C roads to the stream, background water quality data, streambed permeability measurements (mostly via conventional grain-size analysis and slug tests) and undertaking of flow-accretion measurements to determine stream gain and loss (Simpson, 2010, Gamble, 2013). Gamble (2013) undertook a detailed survey of the headwater springs contributing to the Battlefield Brook as well as spot streamflow gauging using a Sensa-RC2 electro-magnetic flow meter calibrated in accordance with the ISO 3455 standards. Gauging was undertaken on 4 separate occasions at 16 different locations along the Battlefield Brook in July 2013 (under summer, relatively low-flow, conditions). A further 2 surveys were undertaken in August 2013 (with slight re-location of some sites to improve monitoring) with repeat (up to 5) flow measurements at each site recorded to improve uncertainty estimates. This allowed a much more conclusive assessment of the gaining – losing condition of the stream than hitherto available (EA, 2010).

3.2. Highways data

Grit (salt) application rates were obtained from the Highways Agency (via Amey plc, Quinton office). Data covered winter periods 2009-10 and 2012-13 for the specific motorway reaches in the study area. The start time and grit application rates of individual grit spreader sorties were obtained. Daily data are presented herein as grams of salt applied per m^2 of highway per day ($g/m^2/d$). Amey plc Quinton office confirmed (Hancox, R., *pers. commun.* [Severe Weather Manager for Area 9 covering the study area]) salt application may involve both treatment with dry salt and pre-wet salt (salt mixed with brine). During the 2012-13 winter, 6 mm salt was provided by the Salt Union salt mines in Cheshire for dry salting and a pure white salt was also used in the saturators for brine manufacture and wet salting. On this basis, it was reasonable to assume that that applied grit mass is 100% NaCl containing 60.6% chloride by mass. This is also assumed by studies elsewhere (Bester et al., 2006; Meriano et al., 2009).

A standard UK motorway is 33 m wide comprising a total of 6 lanes for traffic (3 each way), 2 'hard-shoulder' lanes (paved lanes on the outer motorway edges for emergency use) and a 'central reservation' – the central strip of land separating opposing carriageways (*aka*. the 'median'). All motorway and hard-shoulder lanes are comprised of impermeable 'tarmacadam' (bituminous macadam) pavement. These features are illustrated in Fig. 2 for the M5 where it crosses the Battlefield Brook between our monitoring Sites 3 and 4 that are also shown. In consultation with Amey plc, we have assumed grit application effectively occurs to 7 lanes in that a grit spreader set to maximum spread width covers 3.5 lane widths, i.e., 3 motorway lanes and part of the hard-shoulder lane. Hence overall grit application occurs to a 25.6m (7 x 3.65) width of standard motorway assuming the standard 3.65 m motorway lane width applies. There is some departure from this standard at both the main M5 – M42 interchange in the south of the study area and the motorway junction in the north of the area (near our Site 1 and 2 stream monitoring) that includes four 2-lane slip roads and roundabout infrastructure. The influence of these features on salting area has been approximately allowed for by additional area estimates for these features.

Amey plc also confirmed the reaches of motorway that drained to the various discharge points on the Battlefield Brook shown in Fig. 1. These accorded with topographic expectations. Drains are typically located at frequent intervals within the hard-shoulder lane (or sometimes central reservation) to intercept the highway runoff which is conveyed through an underground pipe network to storm-sewer discharge points to the receiving surface water, the Battlefield Brook. The Fig. 2 motorway, for example, drains and discharges to the brook just upstream of the shown Site 4 locality via the discharge indicated in Fig. S1e (Suppl. Mat.). Motorway lengths discharging to the brook are long: 3.1 km of M5 runoff is collected with storm-sewer discharge occurring to the reach between our monitoring Sites 1 and 2; 2.4 km of M5 discharges between Sites 3 and 4; and, 1.8 km of the M42 and M42 - M5 link discharges between Sites 5 and 6. A total of 7.3 km of motorway hence drains to the stream with the three discharges occurring over a reach length of just 4.0 km, the first discharge being 1.35 km from the stream's source.

The study area also contains a significant network of A and B roads some of which have been confirmed as draining into the Battlefield Brook, but not all, particularly within the southern area due to the urban complexity and effort involved. The more significant A/B roads are in the northern area around our Sites 1 and 2 linking to Junction 4 of the M5. Salt application to A/B roads is largely managed by Worcestershire County Council (WCC) from whom a salt application map has been obtained of primary and secondary gritting routes that is transcribed on to Fig. 1 (WCC, 2013). Salt application rates to these roads were estimated based on professional practice advice with assumptions indicated later in the text.

3.3. Lumped parameter modelling

A daily time-step water mass balance (lumped parameter) Excel® spreadsheet model was developed to simulate water exchange between the various environmental compartments and observed transients in surface water flows. It has been developed for the catchment upstream of Site 3 (Gamble, 2013) and is used to provide volumetric water flow analysis underpinning of the chloride mass balance in Section 4.5.

4. Results and discussion

4.1. Highway salt application

Both 2009-10 and 2010-13 winters received very high salt applications. Cumulative applications to the study area motorway are shown in Fig. 4 for these winters and Table 1 indicates the total winter applications, including the intervening milder winters. Profiles are contrasting, but contain similarly steep gradients when high daily applications of around 40 - 60 g/m^2 of salt to the motorway occur during key snowfalls or prolonged cold. The mild winter 2011-12 application amounted to 38% of the 2012-13 maximum.

Table 2 estimates the road lengths and areas for salted motorway and A/B roads draining to stream reaches A and B (Fig. 1). A total motorway length of 3.1 km and area of over 93000 m^2 drains to these reaches upstream of Site 3. The additional A/B road drainage amounts to a further potential road area of 66500 m^2 giving a total potential road surface of some 160000 m^2 draining to the stream above Site 3. There are some uncertainties over the A/B-road connectivity of more remote road lengths and those (minor) contributions could be overestimated.

4.2. Stream temporal data

The dynamic influence of deicing salt on stream quality is illustrated in the 2009-10 and 2012-13 winter plots of stream flow, estimated stream chloride (from EC), daily motorway salt application and climate data (Fig. 5). The minimum standard (single sortie) salt application shown of 8 - 20 g/m^2/d addresses low to moderate risk of ice due to night-time potential freezing conditons. 30 – 40 to g/m^2/d applications occur when risk of ice or snowfall is moderately high. A typical maximum of 60 g/m^2/d (and occasionally higher) is applied around times of snowfall, persistent snowfall remaining on the highway or severe freezing conditions persisting throughout the day. It is apparent that salt applications are invariably followed by increased chloride cocnentration estimates observed in the stream. Key observations, assisted by letter-labelled Fig. 5 annotation, are summarised below.

During warm periods of increased preciptation, Site 3 stream flow are estimated to potentially exceed 15 Ml/d (note such high flows are indicative per Section 3.1.1). Salt application is occasional and estimated stream chloride low (Fig. 5 label [a]). Natural recession of upper catchment streamflows due to delayed runoff and declining head-dependent baseflows is most apparent in the 2012-13 data labelled [a’]. Assymetric stream chloride peaks with low-dispersion steep fronts are followed by gradual tails attributed to more dispersed runoff from more distant highway or salt less easily flushed from the non-smooth motorway surface micro-porosity. The 2012-13 data exhibited less dispersed peaks that may relate to the reduced highway catchment monitored then. Steep chloride declines were ascribed to precipitation onset causing rapid salt runoff, increased streamflow and dilution ([b] labels).

Marked variation in estimated stream chloride occurred from background *c*. 25 mg/l to over 3000 mg/l (Fig. 5 labels [c]). Such peaks corresponded to a NaCl content of 5000 mg/l, or 15% of sea-water salinity, an order of magnitude above the 250 mg/l national Environmental Quality Standard (EQS) protective of aquatic life (and coincidentally equals the chloride DWS). Peaks occurred typically immediately following snowfall where road salt applications had been increased, or where there was yet further snowfall, or else there were sustained cold conditions with a lack of preciptation as rain. The limited water entering the stream was hence mostly derived from salt-induced melting of highway snow as other precipitation water was largely locked up as snowfall or ice in the wider catchment. Slightly increased stream flows over baseline may be observed at labels [c] and were attributed to ‘packets’ of highway, salt-rich, melt water that induced order-of-magnitude concentration rises in the receiving stream due to the lack of dilution from wider, still frozen, catchment water. Chloride estimates suggest the EQS was exceeded for some 33% of the 2009-10 and 18% of the 2012-13 winter seasons. Exceedence of the EQS by an order-of-magnitude was estimated to occur for 1.5% of each winter.

Direct monitoring of a motorway storm-sewer discharge occurred just upstream of Site 4. Tail-end concentrations of snow-melt runoff events were sampled and found pipe discharges of around 3500 mg/l. Sampling was hence somewhat after the expected peak storm-sewer discharge concentrations. An estimate of this peak was made from a mass balance calculation on observed stream concentrations and flows of 2500 mg/l and 2940 m^3/d at peak label [d] (Fig. 5, 19-Jan snowfall event). Subtraction of the immediately prior 16-Jan concentration and flow contribution of 93 mg/l and 2415 m^3/d estimated an increase of 525 m^3/d flow ascribed to the de-iced water input from highway runoff which in turn calculates a storm-sewer discharge of around 13500 mg/l chloride. This corresponds to 68% of sea water salinity and is potentially illustrative of high concentration discharges that could occur prior to dilution in receiving surface water.

Small spikes of stream chloride were attributed to low-level salt applications intended to address nighttime freezing risks, but rapidly washed off by ensuing rainfall. Label [e] in early

Feb. 2013 flags this behaviour with chloride (and flow) spikes superimposed on a recession curve. Alternatively, salt may persist on the highway and possibly increase with repeated salt applications (recognising on-going losses to the roadside or vehicles) . Labels [f] (and associated arrows) highlight periods of salt application that were followed by delayed, moderately elevated, stream chloride peaks. These instances appeared to largely coincide with dry, clear-sky, sub-zero freezing nights largely mainatined over the arrowed length periods. It is inferred from our delayed stream peaks of chloride relative to salt application dates that accumulated highway salt was being eventually washed off by later precipitation (at the arrow termination dates shown). The April 2013 case shows eventual salt removal by two small rainfall events. It is inferred from this and other highlighted [f] cases that some salt may be persisting on the motorway surface for up to 2 weeks or more. Our very occasional observations did find the motorway could appear whitened in such dry periods that we attribute to the presence of residual salt on the highway surface.

4.3. Streambed transmission of chloride

Downward leakage of stream water containing chloride through the streambed was confirmed by the streambed monitoring data (Fig. 6). Low chloride occurred throughout the early 2009-10 winter Round 1 with a mean chloride of 31.9 ± 8.8 mg/l (Fig. 6c). Salt applications prior were limited and this is regarded as near, but not quite, baseline conditions. Round 2 immediately followed sustained deicing and a 3000 mg/l stream chloride peak. Stream concentrations by then were around 1000 mg/l peaking at Site 4 (Fig. 6d). Stream concentration step-increases of 630 mg/l between Sites 1 and 2, 620 mg/l between Sites 3 and 4, and 220 mg/l between Sites 5 and 6 confirm the incremental motorway discharges with downstream progression. The motorway storm-sewer discharge of 3520 mg/l between Sites 3 and 4, combined with Site 3 and 4 stream concentrations and Site 3 flow, estimated a Round 2 chloride mass flux in the storm-sewer discharge draining 2.4 km of motorway of 1.56 t/d (Supp. Mat., Box 1). Peak mass fluxes, based on the concentration profile immediately prior (Fig. 6a), may be 2- to 3-fold higher.

Streambed piezometer data for Round 2 (Fig. 6d) captured the mid- to tail-end infiltration of high concentration chloride stream water through the streambed. Greater concentrations at depth corresponded with the declining stream concentration of a doublet peak of 3000 mg/l occurring a few hours and 2 days prior (Fig. 6a). Shallow streambed concentrations were comparable with the current stream except for elevated Site 4 values that were posibbly related to its silty, less transmissive, streambed. Round 3 data exhibited similar, albeit reduced, concentration features (Fig. 6e).

Ths Site 3 temporal data (Fig. 6f) demonstrated wide variation in stream and streambed concentrations and dynamic chloride transmission through the streambed. Greater streambed concentrations reflected the transmission of the immediately prior stream chloride peak. Rounds 3 and 4, within 4 d of each other and the observed progression of the 500 mg/l concentrations deeper calculates chloride was infiltrating at around 0.04 m/d.

However, solute streambed velocities were expected to be greater under rising stage and increased streambed hydraulic gradient conditions.

Overall, these data confirm the dynamic infiltration of chloride through the streambed with consequent entry to the underlying aquifer inferred. Downward infiltration of elevated chloride concentrations are expected to be assisted by any density contrasts with lower concentration streambed or underlying vadose zone water. Istok and Humphrey (1995), for instance, observed density effects in homogenous sands at only 50 – 1000 mg/l bromide solutions of very low relative density contrast.

4.4. Stream flow acretion and loss

Stream flow measurements during summer 2013 (Fig.7) demonstrated stream gain from its source until just after the upstream motorway crossing point (Site 2, gauging site G6). The stream then loses water shortly after the Blackwell Fault - Kidderminster sandstone / Wildmoor sandstone contact (Fig. 1). Further downstream over both Wildmoor and Bromsgrove Sandstone Formations, the stream continues to lose water leading to the need for summer flow compensation by an ALF borehole that causes the 2000 m^3/d abrupt flow increase just prior to our Site 3 (EA flow gauge). Without this augmentation, based on the Fig.7 trend, the stream would be projected to dry up a little upstream of our Site 5 monitoring (and did so historically in the early 2000s; Supp. Mat., Fig. S1j).

Sub-reach stream gains and losses estimated from the Fig.7 summer data are summarised in Table 3. Whilst these data are comparable over the specific reaches, greater confidence is placed in the network-enhanced August 2013 monitoring. We hence use the average reach A gain of 0.929 Ml/d/km and average loss in reach B of 0.314 Ml/d/km (megalitre per day loss to the underlying aquifer per km of stream reach) in later calculations. Table 3 and Fig.7 thus quantitatively confirm the stream acts as a line-source of infiltrating water to the aquifer. Increased losing rates may potentially occur in the winter due to increased stream stage and width providing greater gradients across the stream bed and footprint area of influence. We have some preliminary data that support this is the case.

4.5. Chloride mass estimates

Cumulative chloride mass estimates for winter 2012-13 pertaining to the Site 3 catchment are summarised in Fig. 8. The mass conveyed by the stream at Site 3 was calculated from the time-variant product of flow (Q) (Agency flow gauge data) and concentration (C) (logged EC converted to chloride). The Fig. 8 profile indicates an estimated 135 t of chloride equivalent to 223 t of road salt was conveyed by the stream past Site 3 over the winter. However, the above estimates are regarded as somewhat upper- or potential over-estimates due to the observations below.

Our review of the EA flume stage-discharge rating curve suggests there may be some systematic over-estimation of the Site 3 flows. Additionally at flows exceeding 7.5 Ml/d, the

Site 3 Agency flow gauged flows can only be regarded as indicative (per Section 3.1.1). Fig. 5 indicates that although there were significant periods in 2012-13 above the calibrated gauge limit, estimated chloride concentrations were then typically low, either diluted and, or deicing salt application was unlikely. Still, it is probable that flows and hence mass fluxes may be systematically over-estimated. A build-up of silt or debris around the EC probe will also tend to cause artificially elevated EC values and hence, when in this condition, will systematically over-estimate chloride concentrations. This was observed in the end-of-season data in 2009-10 (post 23/03/10, Fig. 5a) due to the silty streambed location of the Site 6 monitoring. This does not appear to be a significant issue for the 2012-13 data due to the move to the less silty Site 3 location. Still, this would not preclude the potential for some transient silting influence on the EC that may remain undetected and result over-estimation of chloride at times.

The stream chloride mass leaked to the underlying aquifer was estimated from the product of the Site 3 chloride concentration temporal estimate (predicted from EC) and the Reach B stream leakage. The latter was based on the (Table 3) August 2013 observed mean of 0.314 Ml/d/km in the absence of an accurate winter estimate. Over the 2.2 km stream reach, the leakage of chloride to the aquifer amounted to 22.5 t. Assuming a background chloride concentration contribution of 25 mg/l, some 19.9 t equivalent to 88% of that amount was attributed to highway salt chloride inputs and is shown as the highway chloride leakage to aquifer profile in Fig. 8 alongside profiles based on minimum and maximum Reach B leakage rates (Table 3) that estimate highway chloride mass leaked to the aquifer was between 15.2 t to 22.1 t. Actual leakages could potentially be higher if winter gradients across the streambed and footprint of influence are increased as postulated in Section 4.4.

A chloride mass (M_{Cl}) balance was used to estimate the highway discharge of chloride mass to the stream from the motorway reach and other A/B roads upstream of Site 3:

$$M_{Cl\text{-}Highway\ discharge\ to\ stream} = M_{Cl\text{-}Stream\ discharge\ at\ site\ 3} + M_{Cl\text{-}Reach\ B\ leakage\ to\ aquifer} - M_{Cl\text{-}Background} \quad \text{Eq. (3)}$$

This estimate of highway discharge of chloride mass to the stream is made independent of the highway salt application data against which it may be compared. The first two (right-hand-side) terms of Eq. (3) are calculated per above with time. Various assumptions can be made to calculate the background mass arising from non-highway sources of chloride contributing to the stream. We use a background concentration of 25 mg/l based on summer – pre winter and upper catchment baseline monitoring and apply three different assumptions on the flow term Q to reasonably cover possibilities: Assumption (i), Q is based on the spring flow estimates of the stream headwaters that are based on the flow model and data of Gamble (2013); Assumption (ii), Q is based on the modelled stream flow leaving reach A (just prior to the stream becoming losing), again based on Gamble (2013); Assumption (iii), Q is based on the flow measured at Site 3, i.e., the end of Reach B. The cumulative background masses calculated over the winter for these assumptions are 4.9 t, 8.3 t and 17.1 t respectively. Cumulative mass estimates of highway chloride discharge to the stream calculated from Eq. (3) for the above three background assumptions are shown in Fig. 8. Estimates range from 144 to 156 t of chloride, equivalent to between 237 t and 257 t of highway salt application.

Salt application to the single 3.1 km of motorway reach and motorway junction (island and northern slip roads) was estimated from motorway gritting records and is shown to amount to 112 t of chloride in Fig.6. This mass estimate is short of the above mass estimates of calculated highway chloride discharge of 144 – 156 t of chloride. This shortfall, also recognising 100% drainage of motorway chloride to the stream was unlikely, points to the potential importance of the A/B road network salt contribution. We plot three possible scenario profiles that simply assume 50%, 75% and 100% of the motorway salt application rates apply to the A/B road network (Fig. 8) that likely encompass the actual application. All of the salted roads are on the primary local authority salting route with the dominant contributions being from the A-roads that serve the motorway junction, in particular the 1.9 km of A38 dual carriageway that also acts as the main trunk road through Birmingham.

Based on communications with relevant practitioners alongside considerations of motorway junction proximity, steep topography and high traffic use of these A roads, it is probable that the 75% application profile is a reasonable middle estimate. It leads to a cumulative winter mass of 172 t of chloride and is shown in Fig. 8 to exceed the stream-based [Assumptions (i – iii)] highway chloride discharge estimates by 20 to 34 t. For the Assumption (iii) case, the calculated discharge to the stream accounted for 80% of the highway salt application with the remaining 20% of the application (34 t) assumed to split between vehicle carry off and lateral loss to the sides of the highways that may also infiltrate to the aquifer. The maximum (100%) salt application profile in Fig. 8 would calculate a split of 72% highway salt discharge to stream and 28% to other losses.

4.6. Chloride mass fluxes

Presentation of Fig. 8 data as chloride mass flux estimates in Fig. 9 provides a clearer indication of the dynamic relationship between salt application and discharge to the stream. Highway salt application profiles for 2012-13 are plotted alongside the chloride runoff storm-sewer discharge to surface water estimated from Eq. (3). In particular, the inferred delayed removal of salt from the highway surface and the close relationship of salt runoff to precipitation become more obvious; for example, the two instances of long-delayed runoff spanning 2 to 3 weeks (label [f] in Figs. 5 and 9). The later season runoff around 14 April is seen to be washed off by two relatively small precipitation events as a doublet of peaks where it appears the first event was insufficient to fully deplete the road surface of salt. The longest delayed salt wash off (mid-February to around 7th March) is also obvious on the Fig. 8 cumulative mass plot as a horizontal line of near zero chloride discharge to the stream set against a rising trend of highway salt application.

The mass-flux plot also makes the inferred persistence of salt on the highway surface of just a few days more obvious (labelled [g] in Fig. 9). For instance, the early season data leading up to mid December 2012 exhibit three broad low-level peaks of salt application washed off by discrete precipitation events. This period in the Fig. 8 cumulative mass plot exhibits a relatively high departure between salt application and discharge mass to the stream. Decrease in the latter is reasonably attributed to greater loss of salt chloride to other, vehicle and lateral roadside, pathways under those prevailing conditions.

4.7. Chloride fate in the study catchment and impacts to groundwater - discussion

Scoping calculations may be made of deicing salt fate within the catchment and its potential to account for increased supply well chloride. Extending from the Site 3 sub-catchment analysis, by Site 6 salt application to a further 4.2 km length of motorway of 112000 m^2 area occurs and adds, in 2012-13, a further 139 t of chloride to the catchment (Table 1). Combined with the Fig. 8 'motorway plus A/B roads at 75% of motorway application rate' mass, the catchment application totals 309 t of chloride, 510 t of deicing salt (application to the more limited A/B local road network downstream of Site 3 is reasonably ignored for simplicity). Assuming, per the Site 3 estimate, that 80% of the highway salt application is discharged to the stream, this calculates at total discharge to the stream of around 247 t. Noting the similarity in Fig. 8 of the observed stream chloride at Site 3 with the highway chloride discharge to stream, this mass is regarded as indicative of the mass conveyed by the stream at Site 6 leaving the catchment. It compares well to our 2009-10 winter EC Site 6 monitoring data that (combined with up-scaled Site 3 gauged flows by relative catchment area (1.62) and also factoring in the increase in motorway salt application in 2012-13 relative to 2009-10 (1.2 times, Table 1)) predicts 250 t of chloride leaving the catchment in 2012-13.

As a first estimate of stream leakage of highway-derived chloride to the aquifer, it may be assumed leakage over reach B also applies to reach C. Their reach stream losses are fairly comparable (Fig.7) and moreover, chloride concentrations at Sites 3 and 6 are broadly similar (Fig. 5, Fig. 6c-e). This may relate to the area ratio of highway network draining to Site 6 compared to Site 3 of 1.7 (272,000 m^2 / 160,000 m^2) being comparable to their corresponding land catchment area ratio of 1.62. Chloride contributions at these sites may thus be diluted to comparable concentrations. Hence using the observed concentration (EC) record at Site 3, the reach B (summer) stream leakage of 0.314 Ml/d/km and the combined reach B and C length of 4 km leads to an estimated severe winter 2012-13 stream leakage of 43 t of chloride of which 38 t is highway-derived chloride. This is equivalent to 63 t of road salt and 12% of the deicing salt applied. Salt applications for earlier years are 32 t for 2009-10, 27 t for 2010-11 and 15 t for 2011-12. Stream leakage may hence account for 21 – 54% of the well chloride increase of 70 t per annum (t/y). There may be systematic underestimation from the use of summer stream loss rates. A doubling of stream loss under say higher stage conditions would make the stream loss contribution much more comparable to the well increase. Also, increased stream leakage could be induced over reach C by the proximity of the southern supply well to the stream (although our observed data do not confirm this).

The above shortfalls point to additional sources of chloride to the supply wells. The non-quantified infiltration of deicing salt lateral to highway is potentially significant and expected based on the aforementioned international literature. The aquifer around reach C and the southernmost well is vulnerable to such inputs, particularly at the motorway cutting through the sandstone (Fig. 1; Supp. Mat., Fig. S1i). Our earlier scoping estimate of 20% (by difference) of deicing salt application being available for lateral highway infiltration, but also vehicle carry off, compares to the low end of the 20 - 63% range for lateral highway infiltration observed by Blomqvist and Johansson (1999) in Sweden. Our UK case conditions may favour a low-end value in that snowfall is not that common, ploughed snow displacement likely remains largely within the paved hard shoulder and pre-salting in advance of ice and snow has been common practice. Moreover, although there has been local gritting fleet capability since 2009 to deliver either dry salting or pre-wet treatments, the pre-wet option (involving dry salt being mixed with pre-prepared brine at the spinner on the gritting vehicle) was much preferred in 2012-13 and would have allowed salt to more effectively target and adhere to the highway compared to dry treatments (Hancox, R., *pers. commun.*). Decreased potential for lateral roadside and vehicle carry-off losses may hence occur. A lateral highway infiltration of 20% would represent 62 t for our 2012-13 salt application and 24 t of the 2011-12 mild winter application. These quantities together with our stream infiltration chloride flux estimate could mostly account for observed chloride increases in the supply wells.

4.7.1. Other chloride sources

Whilst highway deicing salt application in recent years within the catchment has varied from 1.7 to 4.4 times the additional 70 t of chloride annually abstracted by the wells and is perceived the most credible source, other sources outlined in Section 2.4 are possible, none are proven contributors. Concerning well abstraction-induced up-coning of more saline water from depth, this could possibly generate higher fluxes than the other sources, but is more probable in the sandstones further south of the study area. The highway salting depot and landfills are towards the north of the study area and are unlikely to have influenced the southernmost well at least that exhibited the more rapid concentration rise. Available monitoring at one of the lined landfill sites is noted to include a sophisticated geophysical leak detection system within the site liner that has demonstrated highly effective containment.

5. Conceptual model, conclusions and relevance

This study has quantitatively demonstrated that winter leakage to groundwater of a losing stream receiving highway storm-sewer discharges containing deicing salt may constitute a significant line-source of chloride to the underlying aquifer. Fig. 10 provides a conceptual model of deicing salt application pathways to an abstraction well alongside other example chloride sources. The model is anticipated to have generic relevance. Whist the conceptualisation is a simplification of the study scenario, it is illustrative of the complexity of source zone apportionment that may account for chloride increases at a supply well.

Winter deicing salt loading to the aquifer has occurred since motorway opening, coincidental with the 1962-63 main onset of UK salting activity. Loadings will have varied annually due to changeable UK winter severities that may cause applications to differ by over three-fold. Our study confirms aquifer loadings will also daily vary. Pulsed winter-season salt inputs with inherent daily variability are hence conceptualised to the aquifer from the leaking stream (and via infiltration lateral to highways). Such pulsing is unlikely to be evident at supply wells due to dispersive mixing over years to decades in the low-velocity, high-storage, aquifer and also differing transport distances to the well from reach lengths of both leaky stream and highway line-source inputs (Fig. 10).

Whilst challenges were encountered in quantifying chloride mass/flux (notably flow gauge accuracy at high flows, salt loading from other roads, weaker chloride-EC correlations at low concentration), it is perceived these may be largely overcome by modest investment in enhanced data acquisition or minor approach modification. The approaches used are comparatively low-budget with potential utility of combined EC – flow logged measurements to estimate transient chloride (salt) mass fluxes to be more widely used. This may include more intensive deployment over a stream network to resolve spatial complexities, streambed installations to track salt infiltration, and deployment within highway storm-sewer discharge pipes to measure deicing salt storm-sewer discharge fluxes. The latter may represent an important contribution to highways management recognising other fluxes (salt deposition lateral to the highway, salt retention on the highway and vehicle carry on/off) are challenging to dynamically measure (Booth et al., 2011).

Mild and severe winter stream leakage may account for around 21 to 54% respectively of the long-term PWS well chloride increase. Very approximate estimates of deicing salt infiltration lateral to the highway by difference of around 20% were potentially commensurate with low end values within the international literature. Taken together, these deicing salt contributions could account for most, although probably not all, of the chloride increases at the wells. Whilst the contribution of other anthropogenic or natural (geological) chloride sources may still be (locally) significant, continued effort to assess the relative balance of deicing salt infiltration to the aquifer via stream leakage versus porous ground lateral to the highway is considered a priority over the consideration of other chloride sources. The annual mass of deicing salt imported to catchments remains very high and likely to significantly exceed other anthropogenic inputs.

PWS well chloride in the high-storage, thick-sandstone, aquifer remains far below drinking water standards in spite of the high deicing salt loading. This observation confirms the relative importance of dilution by low-chloride recharge contributions within the wider capture zone. Some aquifers, for example low-storage, low recharge or more urbanised systems, however may be more susceptible and increased understanding of deicing salt fate ultimately prove relevant. Despite climate change-based predictions of reduced salting for the UK, applications in the studied severe recent winters were likely in record-breaking amounts for many UK areas and further underscore the need for improved salt fate understanding.

Whilst the study was motivated by vulnerable groundwater concerns, deicing-salt loads were primarily born by the surface-water. Around 80 % of the storm-sewer de-icing salt discharge (and majority of highway salt applied) remained in the stream. Stream chloride exceeded the EQS for 18 – 33% of the severe winters and peaked at 15% of sea-water salinity. Although winter salt loads are often presumed to rapidly flush from catchments and become increasingly dilute further downstream, the (transient) presence of above chloride EQS water may still prove significant and merit study (Cañedo-Argüelles et al., 2013). Sensitive settings may include (combinations of): streams/rivers of high ecological value; smaller receiving streams characterised by low flows and dilution capacity; low-velocity infiltrating streambed or hyporheic zone exchange waters; and, stream water entry and persistence within connected wetland/lake ecosystems.

Finally, the study is relevant to the increased adoption of sustainable urban drainage systems (SUDS) and other highway drainage-to-ground schemes that have become increasingly common. The lack of attenuation of conservative chloride poses concern and schemes should carefully predict the long-term increased salt loads to groundwater resources, especially as problems are slow to manifest and not easily rectified. Deliberate adjustment of the relative surface-water – groundwater loadings of de-icing salts demands careful, integrated and interdisciplinary consideration.

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Supplementary Material

Supplementary Material referred to in this manuscript may be found at ^^^web address^^^^ [Journal to provide phrase].

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Tables

Table 1. Summary of winter season salt application to study area motorways (Highways Agency data provided by Amey plc) The application per km of motorway assumed a 3.65 m lane width with 3.5 lanes gritted (incl. 0.5 for hard shoulder) in each direction and hence 7 lanes are gritted overall and a 25.6 m gritting width for a standard motorway assumed.

Winter	Total Salt (NaCl)	Total Chloride	Total Salt (NaCl)	Total Chloride
	g/m^2	g/m^2	tonnes / km	tonnes / km
2009-10	1720	1042	44.0	26.7
2010-11	~1470	~891	37.6	22.8
2011-12	~782	~474	20.0	12.1
2012-13	2042	1239	52.3	31.7

Table 2. Estimated highway lengths and areas for salted motorway and A/B roads within the catchment and thought to drain to stream reach A (above Site 1) and reach B (from Site 1 to Site 3).

		Draining to Reach A		**Draining to Reach B**		**Draining to Reach A + B**	
Road Type	Road width*	Road length	Road area	Road length	Road area	Road length	Road area
	m	m	m^2	m	m^2	m	m^2
Motorways							
Motorway	26.6	0	0	3100	82460	3100	82460
Motorway junctions (incl. slip roads, islands)	varies	0	0		11224		11224
Total Motorway		0	0	3100	93684	3100	93684
A/B Roads							
A-Road Dual Carriage Way (A38)	14.6	1520	22192	670	9782	2190	31974
A-Road Single Carriage Way	7.3		0	2200	16060	2200	16060
B-Road Major	6.75		0	1300	8775	1300	8775
B-Road Minor	6		0	1620	9720	1620	9720
Total A/B Roads		1520	22192	5790	44337	7310	66529
Total Motorway and A/B roads			22192		138021		160213

* Typical widths of A/B roads based on Newcastle City Council (2011) data.

Table 3. Stream bed gain and leakage rates estimated from reach spot flow gauging in summer 2013 (a negative sign indicates stream loss to the underlying aquifer).

Reach	Gain (loss shown as negative) m3/d/m or Ml/d/km							
	July 2013					August 2013		
	5 July	10 July	14 July	19 July	Average	8 Aug	27 Aug	Average
A	1.049	0.736	0.777	0.920	0.870	0.913	0.945	0.929
B	-0.310	-0.240	-0.255	-0.349	-0.289	-0.263	-0.366	-0.314
C	-0.198	-0.106	-0.264	-0.203	-0.193			
D	-0.303	-0.729	-0.389	-0.266	-0.422			

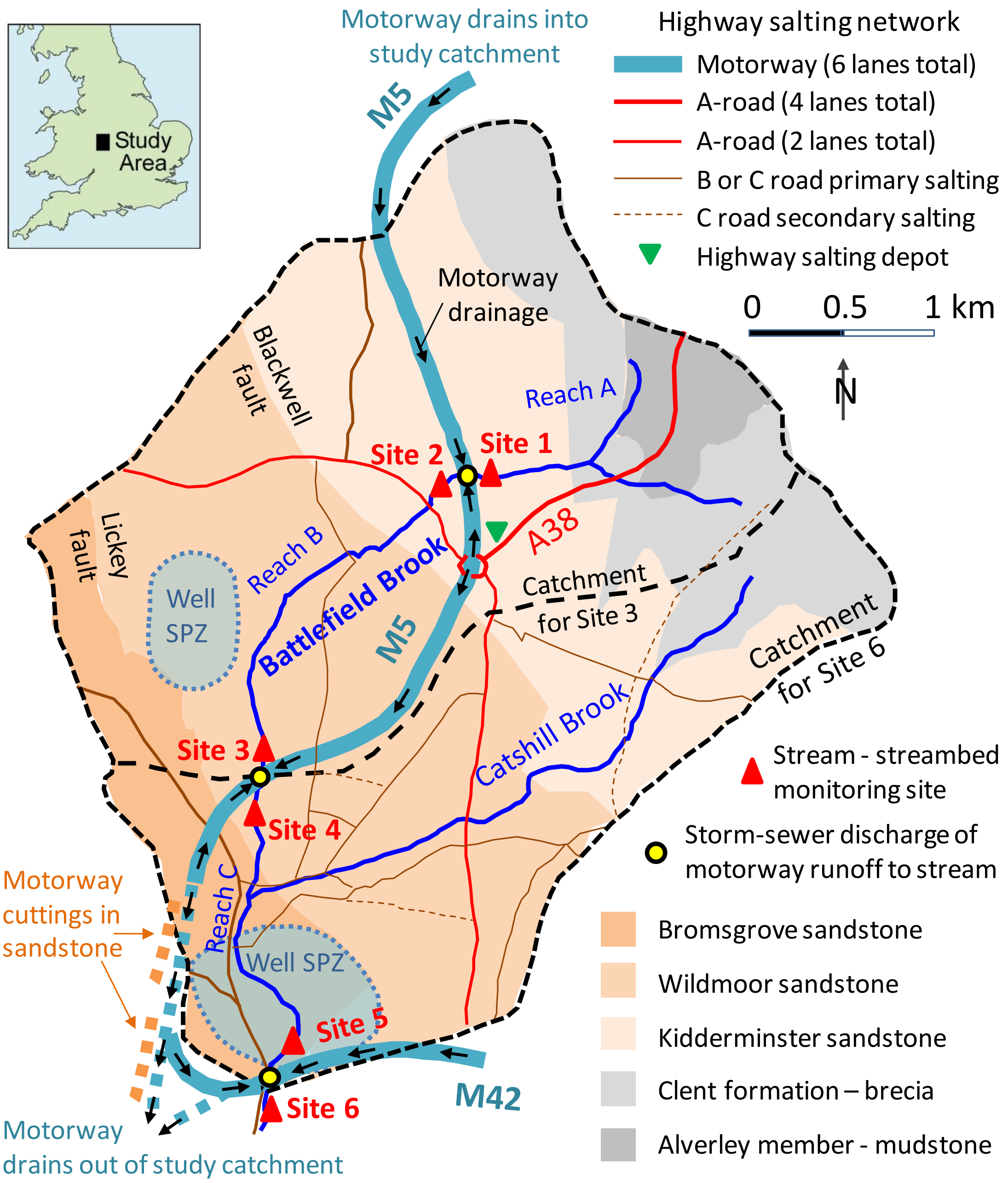


Fig. 1. Study area catchment showing the solid geology (EA, 2010), monitoring Sites 1 – 6, supply well outer source protection zone ('Zone 2'), the salted highway network including motorways and the local road network salted by the Local Authority (WCC, 2013) and the engineered storm-water drainage flow directions to the motorway storm-sewer discharge points on the Battlefield Brook. The named faults approximately track along the immediate geological contact lengths.

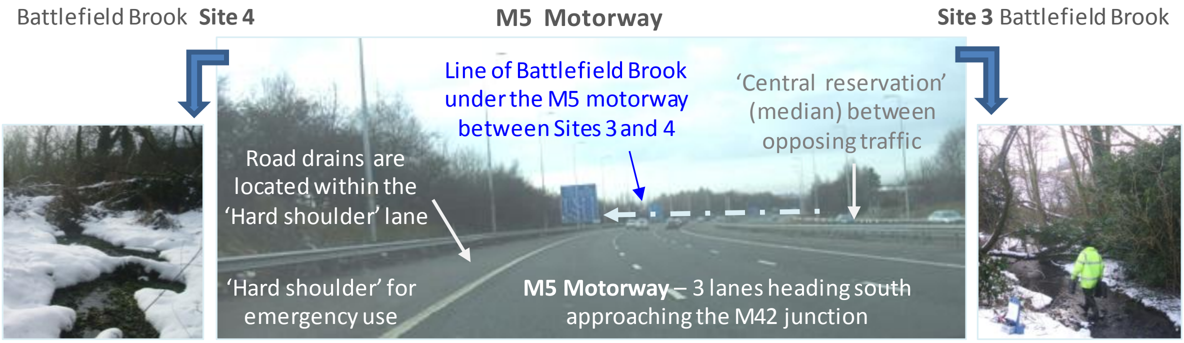


Fig. 2. Photographs showing the elevated section of the M5 motorway between our monitoring Sites 3 and 4 on the Battlefield Brook that passes beneath the motorway within a piped culvert.

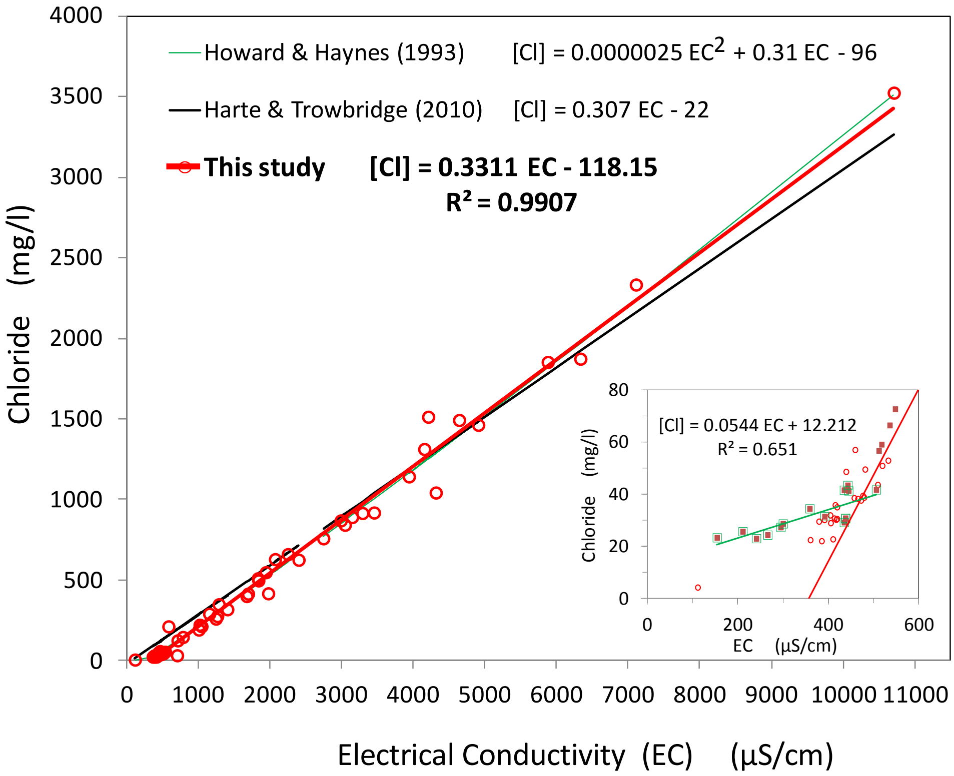


Fig. 3. Correlation of observed water sample chloride concentration with EC compared to correlation trend-lines found for studies elsewhere (the inset shows an alternative fit for low concentration data).

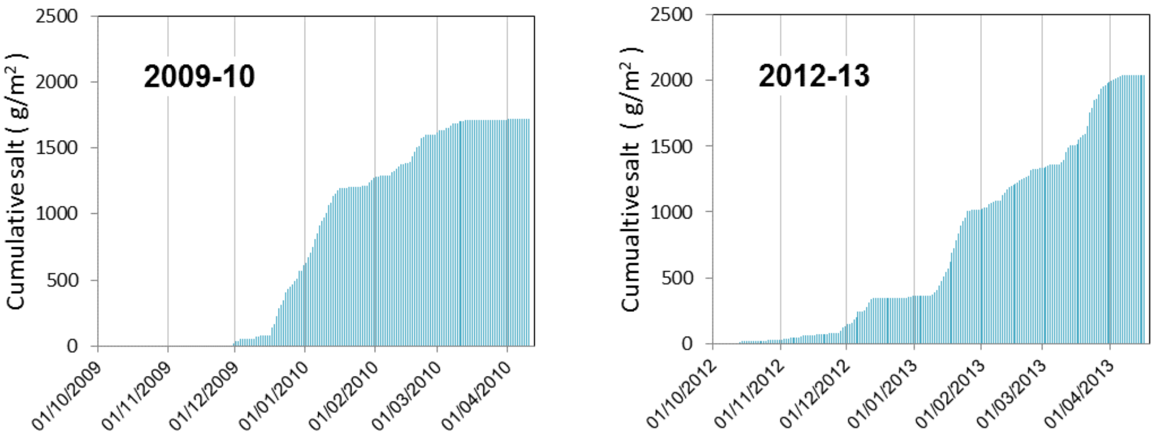
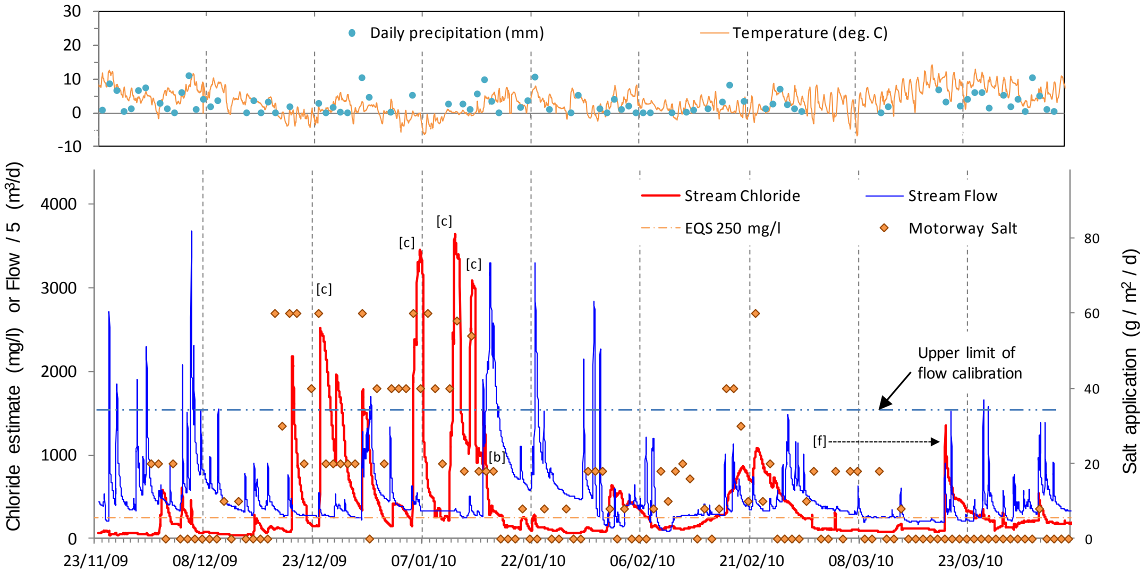


Fig. 4. Cumulative salt (as NaCl) application (g of salt per m^2 of motorway surface) to the motorway network in the study area for 2009-10 and 2012-13 winters based on Highways Agency daily grit application data provided by Amey plc. .

a) Winter 2009-10



b) Winter 2012-13

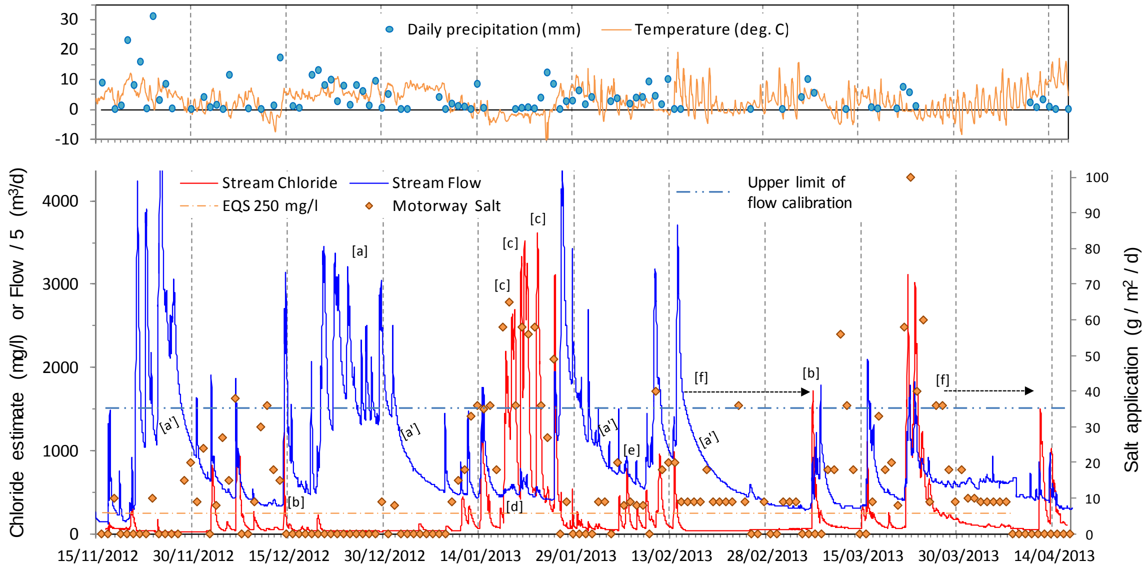


Fig. 5. Winter 2009-10 and 2012-13 data showing: air temperature and daily precipitation (EA data); estimated stream chloride (from logged EC) at Site 6 in 2009-10 and Site 3 in 2012-13; stream flow at Site 3 (EA data) (actual flows are divided by 5 to allow plotting); daily motorway salt application per m^2 of road surface (Highways Agency data provided by Amey plc); chloride EQS of 250 mg/l. Labels [a] to [f] are discussed in the text.

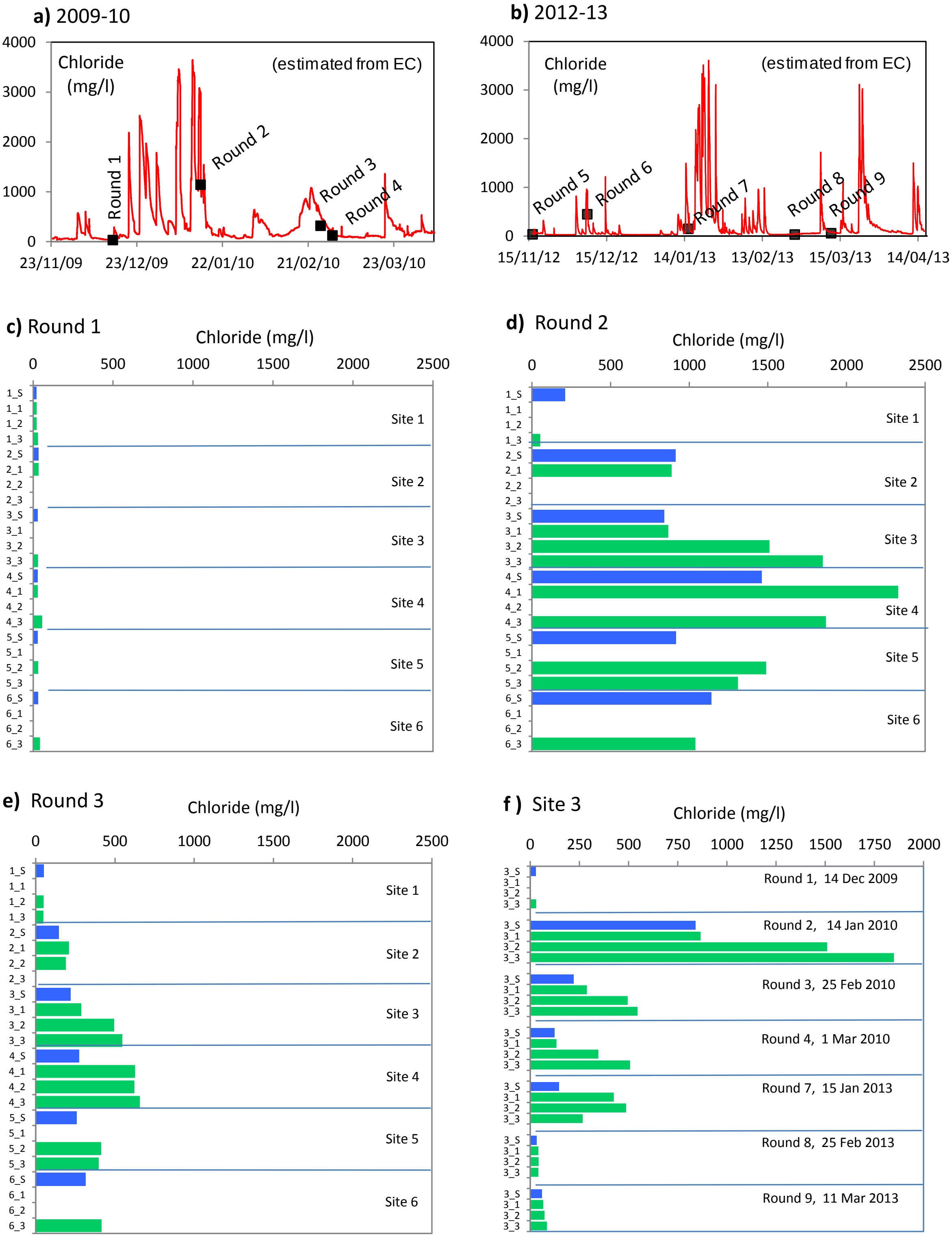


Fig. 6. a) 2009-10 Site 1-6 sampling round timing shown on the Site 6 stream chloride concentration estimate; b) as for a) but for 2012-13 and Site 3 stream chloride; c) to e) Sites 1 – 6 chloride concentrations observed in the stream and underlying streambed profile (y-axis, for example, for Site 1, sample 1_s is the stream sample and 1_1 the shallowest and 1_3 the deepest streambed sample); f) Site 3 data for all sample rounds.

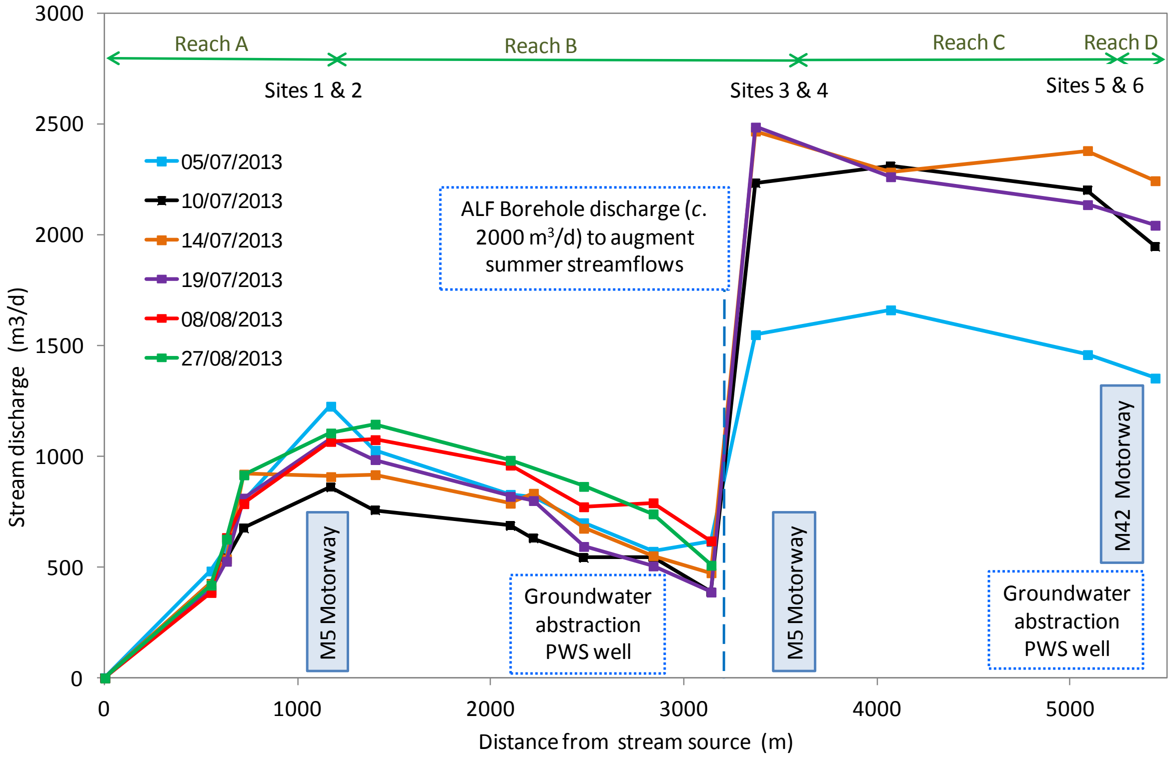


Fig.7. Battlefield Brook stream discharge observed over the study area reach during summer 2013. Motorway crossing points and position of wells (normal to and at varying distance from the stream) are indicated.

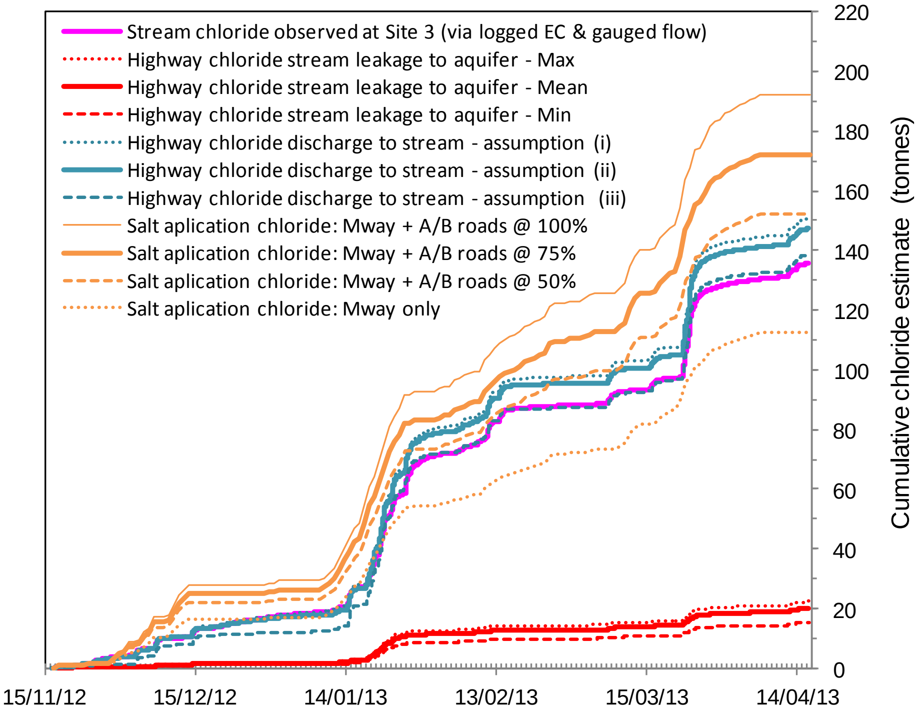


Fig. 8. Winter 2012-13 cumulative chloride mass estimates for observed stream chloride at Site 3 and variants of: highway chloride stream leakage to the aquifer; high chloride discharge to the stream; and, salt application to the motorway (Highways Agency data) and A/B roads as a percentage of motorway application rates.

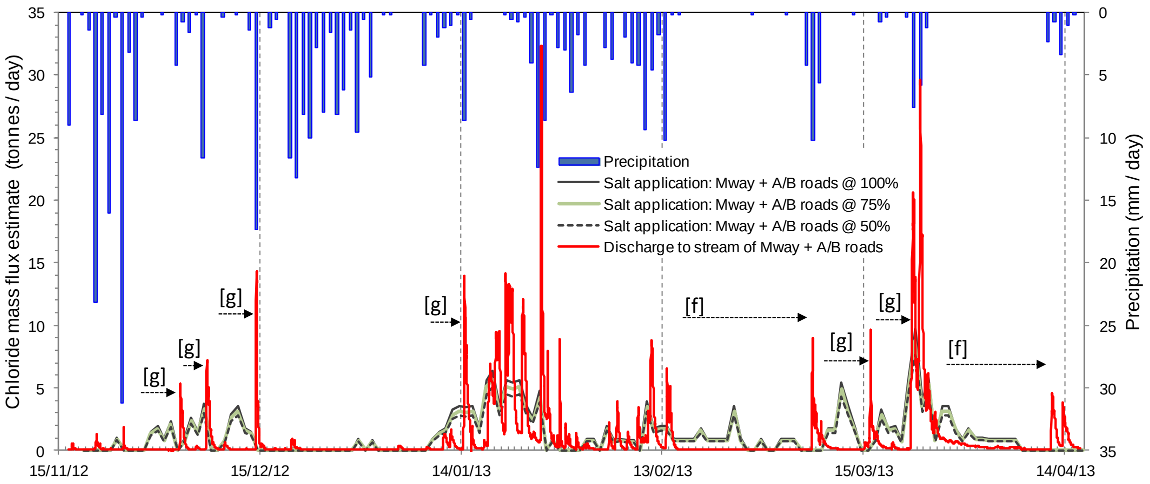
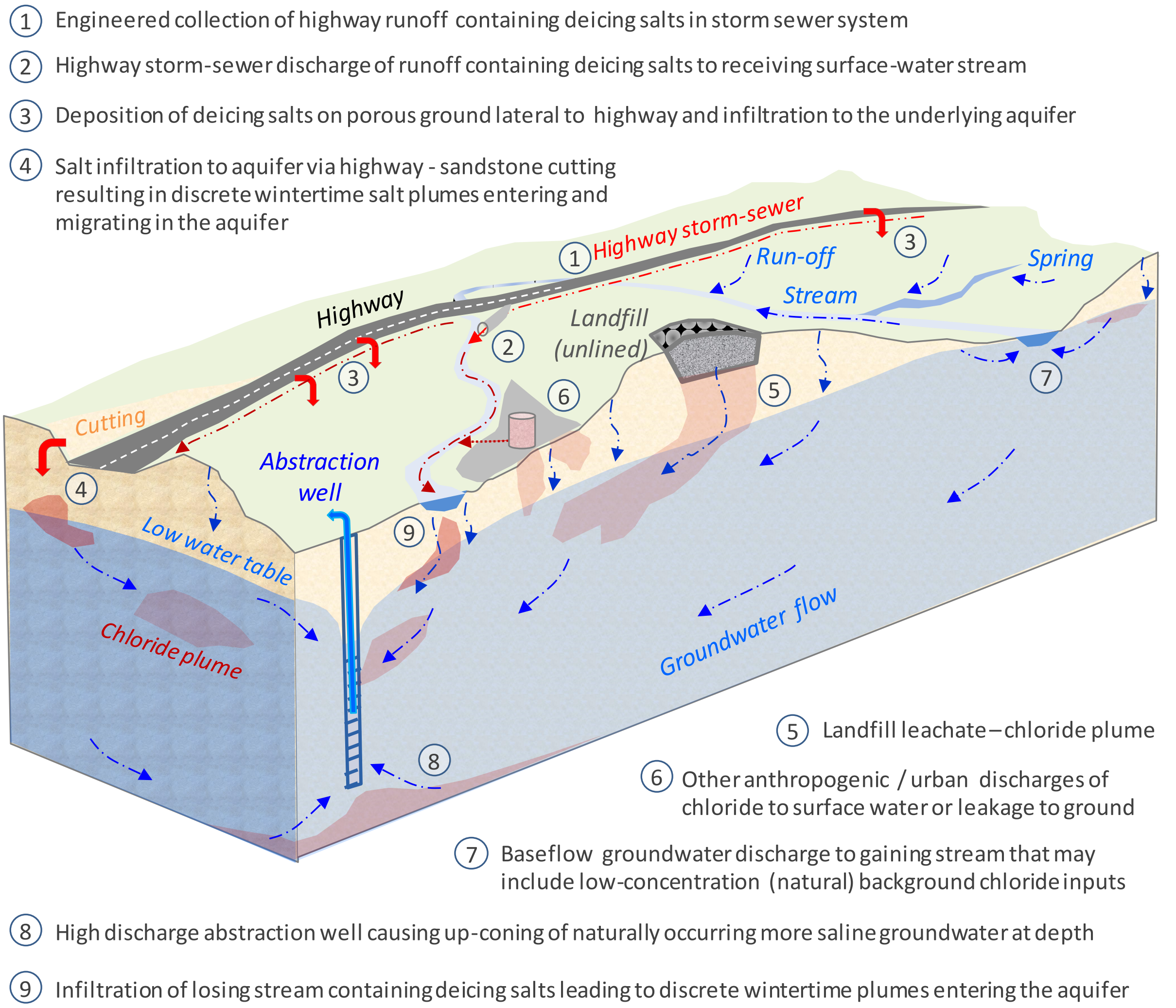


Fig. 9. Winter 2012-13 chloride mass flux comparison of highway runoff discharge to stream (estimated from Eq. (3) and observed stream data) with various highway salt application estimates and daily precipitation data. Labels [f] and [g] are discussed in the text.



① Engineered collection of highway runoff containing deicing salts in storm sewer system

② Highway storm-sewer discharge of runoff containing deicing salts to receiving surface-water stream

③ Deposition of deicing salts on porous ground lateral to highway and infiltration to the underlying aquifer

④ Salt infiltration to aquifer via highway - sandstone cutting resulting in discrete wintertime salt plumes entering and migrating in the aquifer

⑤ Landfill leachate – chloride plume

⑥ Other anthropogenic / urban discharges of chloride to surface water or leakage to ground

⑦ Baseflow groundwater discharge to gaining stream that may include low-concentration (natural) background chloride inputs

⑧ High discharge abstraction well causing up-coning of naturally occurring more saline groundwater at depth

⑨ Infiltration of losing stream containing deicing salts leading to discrete wintertime plumes entering the aquifer

Fig. 10. Conceptual model of deicing salt application and other potential sources of chloride that pose risks to a supply well.