Journal of Knowledge Learning and Science Technology
ISSN: 2959-6386 (Online)
2026, Vol. 5, No. 3, pp. 16–37
DOI: https://doi.org/10.60087/jklst.vol5.n3.002
Journal homepage: https://jklst.org/index.php/home

Measuring Hydrogen Sulphide (H_2S) Gas in The Air of The Refinery And around the Refinery in Erbil – Iraq

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Abstract

The aim of this study is to publish the measurement results of hydrogen sulphide (H_2S) gases both inside and around petroleum refinery complex, and study the environmental and social impacts of the results, in the town of Erbil (Kurdistan Region of Iraq). These measurements were made at twelve monitoring stations at an equal distance (0–5 km) from the refinery and analyzed for a period of twelve months, with analysis also examining the output of AERMOD dispersion modelling and a hazard quotient framework. The results demonstrated that the on-site mean concentrations are above international occupational exposure and community exposure guidelines and that concentrations are a function of the distance from the source source, varying exponentially but concentrations remain significantly higher than the odour detect levels in the residences of the community ring. Winter and night time are periods of time when atmospheric stability will make for much greater exposure. The study highlights that the emissions generated in the refinery activities represent an externality which is not internalized and provides policy suggestions with regard to the need for buffer-zone regulation, monitoring infrastructure over the years and the prioritization of investment for the abatement.

Keywords: *Hydrogen Sulphide (H_2S), Air Pollution, Air Quality, Refinery, Petroleum Refinery ,Gas Concentration, Environmental Monitoring, Occupational Health and Safety Industrial Air Pollution, Erbil, Iraq*

Article information: Received: 01/08/2026; Accepted: 20/08/2026; Published: 25/09/2026

1. Introduction

The Kurdistan Region of Iraq benefits from petroleum refining techniques both economically and environmentally, which is its main drawback. A currently (over the last two decades) developed refining corridor around Erbil refines predominantly sour crude and hydrogen sulphide (H_2S) is a process intermediate which must be removed in the desulphurisation of sour crude. If the recovery trains, flare systems and wastewater separators are undersized or maintenance problems exist or they are sometimes shut to the seawater, there is a significant amount of H_2S lost to the air before it turns into elemental sulphur. This results in an ongoing exposure burden that is high in one area and occurs over time, but to refinery workers first, and to the area surrounding them second.

Hydrogen sulphide is somewhat of an outlier when it comes to the air pollutants emitted as a result of a refinery's operations. It is extremely toxic at very small amounts, which is much lower than the "signature" of deposition or a visible/particulates pollution component, and its subitizable detection level is several orders of magnitude below its toxic level. This means that communities do not know what has happened until long before conventional regulatory monitoring detects an exceedance, leading to the characteristic "exceedance dynamics" - understanding the community's experience of air quality but not the authorities' reporting of the same. The mismatch in institutional environments with insufficient ambient monitoring skills equates to an accountability gap - harm is real, continuous and formally undocumented.

Recently, the amount of literature published on Iraq and the Kurdistan Region regarding the environment, in general, has increased significantly, while the literature on H_2S is still rather limited. The distribution of nitrogen dioxide (NO2) and sulphur dioxide (SO2) and particulate matters in the region, which includes Erbil was mapped with the help of satellites [1], [2], [22]. There are several studies focusing on the soil contaminations around both refineries, quantifying the levels of PAHs and heavy metals in the immediate vicinity of both refineries [3], [4]. There are also street-dust surveys that show high loadings of metals in the Erbil metropolitan area [5]. Very little information exists, however, of a ground-trusted, times-resolved measurement campaign carried out in obtaining the answer to the single pollutant (also found by the neighbours of refineries quite consistently) that is the source of their complaints.

For reasons other than atmospheric science, this gap is of interest to us. Refinery emissions are textbook negative production externality, that is, costs and benefits of continuing to process a lower-performing sulphur recovery unit (SRU) accrue to very low levels of the private sector, while costs and benefits of the iatrogenic effect of exposing others to the emissions namely, respiratory morbidity, avoidance behaviour, depressed residential land values and lost labour productivity accrue entirely to third parties. Without measured concentration information, the social cost cannot be calculated, or assigned to an individual operator, and can't be internalized via permitting, pricing or liability. There is a relationship between measurement and regulation, and regulation and efficient abatement: Efficient abatement requires regulation, which requires measurement.

To overcome this situation, a measurement campaign was carried out for the first time in a period of 12 months inside and outside the Erbil refinery complex where the H_2S measurements were conducted. It has a focus on four aims. First, to calculate the ambient concentrations of H_2S in space in this case, within a 0 to 5 km distance from the fenceline of the refinery, and time, in both frequency and severity. Secondly, to pinpoint the conditions when the exposure is being exacerbated. Third, to compare the observed concentrations with the international recommendations for exposures in the workplace and community, and to describe the non-cancer health risk from exposure. Fourth, to turn these physical elements into a socio-economic and policy context that can help guide and specify regulation and monitoring of investment and abatement prioritisation in the Kurdistan Region.

The rest of the paper is organized as follows: Section 2 builds up the conceptual background and literature review of the H_2S generation, the health effects, and evidence of regional pollution and measurement of H_2S. The study area, the design for the monitoring, instrumentation, the modelling procedure and the strategy for the analysis, are presented in Section 3. The findings from Section 4 can be found in this section. The implications they have and their comparison with similar studies are described in Section 5. The policies recommended in Section 6, and the agenda for future research, follow.

2. The Conceptual Framework and Literature Review

2.1 Hydrogen Sulphide Generation and Release in Petroleum Refining

The other sources of Hydrogen sulphide in the refinery mass balance are from the Hydrodesulphurisation of the fragrant fractions of sour crude where the sulphur is in an organically bound form is converted to H_2S which is removed from the Hydrocarbon stream. Neutral operating mode in where this stream is sent to an amine absorption unit and then onwards to a Claus sulphur recovery unit, where the achievable recovery rates are in the super ninety-five per cent. There are four major places where loss can happen: In the recovery train inadequate conversion, loss from tail-gas vent at upset conditions, loss from flaring sour gas at conditions that exceed the capacity of the recovery train, and fugitive from wastewater separators, storage tanks, valves and flanges.

Such pathways and their relative importance is heavily influenced by management as well as technology. Comparative work indicated that refineries with a standardised environmental management system would release significantly less material H_2S air compared to other similar refineries that do not have such an environmental management system, with the primary cause of the difference being maintenance discipline and the frequency of leak checks, and not dependency on capital equipment [6]. The second one is controllable -optimisation studies have shown that seasonal management of the flares, based on the prediction from artificial intelligence, can help reduce the routed amount significantly, without affecting process safety, in the Kirkuk refinery [7]. Previous monitoring of the Al-Daura refinery also revealed that the effect of desulphurisation technology on the dispersion profile of pollutants around the refinery was measurable [8].

One unique and regionally significant pathway of release is informal refining. The unlicensed and semi-licensed plants have no recovery facilities at all, with the vented sour gas emitted directly. In the Kurdistan Region currently, both surface and groundwater are contaminated as a result of these operations, while there has been a rise in local environmental activism triggered by them [9]. Similar evidence exists from the Niger Delta where local refining activities result in a positive consequence of respiratory symptoms in neighboring communities [10]. All measurements along the Erbil corridor are therefore a combined signal from the formal and informal sector.

2.2 Predicting the Health Impacts of Anthropogenic Exposure

HS is dose dependent over a very broad range of toxicity. The olfactory nerve paralysis is rapid at a few hundred ppm, respiratory arrest occurs; at a few ppm, which are more typical for community exposures, effects are more subtle, chronic and much more debatable. As the most recent synthesis of the low-level exposure literature, the findings presented here suggest that emissions, community levels of exposure, and health effects have been much less extensively studied than warranted by the number of humans exposed, and that exposure-based guidelines are not as widely based on as is often believed. [29]

The epidemiological findings from geothermal areas, where chronic ambient exposures to H_2S can be found at concentrations similar to that experienced in refineries, are most definitive in providing a signal. In Rotorua, New Zealand, population studies have reported that exposure to ambient H_2S concentrations is associated with self-reported asthma and asthma symptoms [11] while a follow up study examined lung function, asthma and chronic obstructive pulmonary disease [30] in the same population. In terms of studying exposures for oil field workers, subchronic exposure to low levels of these VOCs also generates a similar image that is not fully resolved in doses, with some neurological and respiratory effects lasting only short-term in oil field workers exposed to low levels of these VOCs [12], and long-standing concerns about cumulative cases in oil field workers exposed to low levels of these VOCs remain unresolved [13].

Variations in the regulatory benchmarks that could be based on this evidence base exceed more than an order of magnitude depending on the length of exposure and the philosophy regarding protection used by the regulatory body. The main reference values for the present study are summarised in Table 1

Table 1: Principal International Reference Values for Ambient and Occupational Hydrogen Sulphide Exposure

Issuing Body / Basis	Averaging Period	Value (µg/m³)	Protective Intent
WHO air quality guideline	24 hours	150	Prevention of eye irritation and respiratory effects in the general population
WHO odour annoyance threshold	30 minutes	7	Prevention of substantial odour nuisance
US EPA inhalation reference concentration (RfC)	Chronic (lifetime)	2	Lifetime exposure without appreciable non-carcinogenic risk
ATSDR acute minimal risk level	1–14 days	≈ 98	Prevention of acute non-carcinogenic effects
ATSDR intermediate minimal risk level	15–364 days	≈ 28	Prevention of intermediate-duration effects
ACGIH threshold limit value (TWA)	8 hours, occupational	≈ 1 400	Protection of the healthy adult worker

Issuing Body / Basis	Averaging Period	Value (µg/m³)	Protective Intent
ACGIH short-term exposure limit	15 minutes, occupational	≈ 7 000	Prevention of acute irritation at work
NIOSH ceiling limit	10 minutes, occupational	≈ 14 000	Ceiling not to be exceeded at any time

Source: Compiled by the authors from the exposure-guideline synthesis in Batterman et al. [29]. Occupational values converted at 1 ppm ≈ 1.4 mg/m³ (25 °C, 101.3 kPa).

2.3. Exposure To Air Pollution and To Refinery Pollution in Iraq

Empirical air quality basis has expanded significantly in the case of Iraq due to satellite retrievals. The air quality has been assessed in Erbil and its impact on the surrounding area using remote sensing techniques through Google Earth Engine and geographic information systems (GIS) [1], and a pan-national analysis of air pollutants using Sentinel-5P has been done to map the distributions of main air pollutants and their major source areas [22]. In fact, there have been attempts to map baseline contamination trends throughout the country using a combination of remote sensing and geospatial analysis [2] and in the case study of Baghdad, to better understand what factors are driving the dynamics of air pollution in a riverine megacity environment [14].

Only a few data are available for ground-level in the vicinity of refineries and these have focussed on soils rather than air. The results of modelling guided sampling around the Erbil and Kirkuk refineries showed high levels of polycyclic aromatic hydrocarbons in the surrounding soil [3] and the results of sampling along Erbil Gwer road confirmed the existence of a persistent contamination of the soil with heavy metals and total petroleum hydrocarbons, which were also measured in plant tissues [4]. Previous environmental site assessment of Al-Daura refinery, revealed the level of pollutions in soils due to petroleum products [15]. The contamination level, mineralogical status of these streets and associated health hazards were reported in the Erbil metropolis by the street-dust surveys [5].

The picture is completed by the institutional and methodological studies. As regards the environmental conditions of oil and gas sectoral governance, both PESTLE and SWOT analysis of oil and gas scenario in Kurdistan Region had been done in order to identify the environmental factors [16] and rapid impact assessment matrix approach had been applied to Iraqi industrial organisations in order to structure environmental impact assessment where data are incomplete [21]. In the present study, there is a methodological precedent that is directly relevant to the study being undertaken: Ameen and Azmi [23] is a traffic pollution impact assessment model developed for Kirkuk that was modeled using a Python implementation of AERMOD and GIS. Combined, this literature demonstrates that the refining corridor has been established as a source of polluting emissions, and says nothing about the amount of H_2S in ambient air.

2.4 Environmental Measurement Methods

Most of the current H_2S measurement techniques are based on three families. Significant progress has been reported in the sensitivity and selectivity of resistance-type metal-oxide nanostructures (NS) sensors [17] and nanomaterial-based sensors in general for selective detection [27] which are suitable for dense networks and provide continuous monitoring. They have a main drawback: cross sensitivity and basic drift which demands careful recalibration. Chromatographic methods are the reference standard, catalytic oxidation (collective) gas chromatography with pulsed amperometric detection has high sensitivity and reliability for the quantification of trace H_2S in air and works well for calibrating the reading of continuous sensors [28]. The current standard practice is for combined design where the temporal record occurs with continuous sensors and the accuracy obtained in the periodic chromatographic samples anchors the accuracy of the temporal record.

The dispersion modelling enables the use of point measurements to predict the values of unmonitored receptors. The steady state Gaussian plume model U.S. Environmental Protection Agency AERMOD has successfully been validated over a variety of H_2S applications. It has been used to model and simulate the emissions from sewage treatment in the arid climate of Muscat, Oman with similar complex urban topography to Erbil [18], to assess the emissions from recycled paper mill in Malaysia where field quality measurements were compared to the model output [19], and in regional air quality evaluations in other parts of the Middle East [24]. Complementary computational fluid dynamics (CFD) studies have demonstrated that the location of the buildings in the industry can significantly impact the dispersion of unorganised releases of hydrogen sulfide (H_2S) and influence the receptors where they will be placed [25]. More recently the routine exposure has been differentiated from extreme-event conditions in modelling of community exposure in urban industrial areas, which shows that the annual average exposure significantly underestimates the episodic exposure [20]. Atyrau Kazakhstan has an example of monitoring of urban air near an oil refinery, with the H_2S content in the urban airanalysed under climate and industrial conditions similar to the ones in UAE [26]. The concentrations reported below best reflect the concentration found in that study.

2.5 Environmental Policy Framework

Decisions on whether H_2S physical measurements should become part of the policy debate are only policy-relevant when set in an economic framework. The harmful effects that the emitters incur on other parties constitute a negative production externality which is the generic form of externalities because the private MC curve of the emitter does not include the costs it imposes on the others, the emitter's output turns out to be greater than the socially efficient one, and the differences remain since the external harm questions are too costly for the others to be effectively involved in negotiations with the emitter for reductions. There are three reasons why the problem gets exacerbated by the particular nature of H_2S.

First, at the relevant doses, the damage is diffuse and non-fatal which limits the amount of litigations and maintains the expected damages associated with emissions low. Second, the pollutant itself is not perceived, there are no known health impacts at the individual level - even if the population impact is generally accepted. Third and most important for the present study, as the externality is not recorded, there is no measured externality magnitude and the unmeasured cannot be priced, permitted or litigated. The Kurdistan oil and gas industry is flagrantly and specifically characterized by a lack of monitoring and enforcement ability [16].

The background measurement is definitely much more than simply a scientific experiment, but the determining factor for the complete regulatory chain. This study is hence viewed as an economic input: the empirical “soil” foundational for the buffer-zone standards to be built on, the emission permits to be built on, the abatement subsidies to be built on and of course the damage assessment to be built upon.

3. Materials and Methods

3.1 Study Area

The study took place within and near a complex of petroleum refineries in the industrial area to the West of Erbil, the capital of the Kurdistan Region of Iraq. The city itself lies in a moderately elevated semi-arid plain where hot dry summers and cool dry winters with a definite dry season from May to October are experienced. It is mainly northerly (north-west) throughout most of the year with a secondary southerly (south-easterly) flow in winter during frontal passages. A fundamental aspect of exposure patterns described below is that winter is associated with frequent temperature inversions that are at night and early morning, trapping pollutants in a shallow surface layer of the air.

During part of the year the refinery area is upwind from major residential development, and is adjacent to agriculture and scattered settlement throughout. Measurable deposition of hydrocarbons and heavy-metals has been identified in this corridor as part of previous soil sampling along the Erbil–Gwer road [4]; and modelling work indicated that it is a zone of elevated accumulation of polycyclic aromatic hydrocarbons [3], both of which demonstrate that the receptor environment is already subject to a documented deposition burden of industry.

3.2. Monitoring Network and Sampling Design

A source centred radial design was used to set up a monitoring network with twelve stations. There were three stations inside the perimeter of the refinery, adjacent to the main suspected release areas, and nine stations on, or near, four distance rings, nominally 0.5, 1.0, 2.0, 3.5 and 5.0 kilometres from the refinery fenceline, with individual stations located in different distance rings based on the prevailing wind sector and the location of sensitive receptors. Ashes were collected at two stations located in the upwind sector to act as a regional background station. Table 2 summarises the network.

Table 2: Characteristics of the Twelve Ambient Monitoring Stations

Code	Station Setting	Distance (km)	Sector	Height (m)	Dominant Receptor Type
S1	Sulphur recovery unit perimeter	0.0	On-site	3.0	Occupational
S2	Wastewater separator area	0.0	On-site	3.0	Occupational
S3	Flare stack downwind apron	0.0	On-site	3.0	Occupational
S4	Refinery access road	0.5	NW	3.0	Occupational / transit
S5	Perimeter agricultural plot	0.5	SE	3.0	Agricultural labour
S6	Roadside settlement edge	1.0	NW	3.0	Mixed residential
S7	Residential cluster A	2.0	NW	3.0	Residential
S8	Residential cluster B	2.0	SE	3.0	Residential
S9	Primary school compound	3.5	NW	3.0	Sensitive receptor
S10	Health centre forecourt	3.5	SE	3.0	Sensitive receptor
S11	Regional background (upwind)	5.0	SW	3.0	Reference
S12	Regional background (upwind)	5.0	S	3.0	Reference

Continuous twelve-month sampling resulted in hourly-averaged concentration data for each station each month. This period was chosen to be able to capture the whole seasonal cycle and to allow annual statistics to be calculated which could be compared to the averaging periods of the reference values for Table 1, which span the whole winter inversion season.

3.3 Instruments and Analytical Techniques

The design was decided on to be a dual-method design, consistent with best practice at the time. Electrochemical H_2S analysers (with nominal detection limits of 1 µg/m³) took continuous measurements in temperature controlled enclosures, with a time resolution of 1 minute, which were then hourly averaged. The choice of sensors was determined by the progress made in resistance-based and nanomaterial-based detection as described by the authors of reference [17] and reference [27] as well as the need to deploy the sensors network-wide at an acceptable cost.

Ion chromatography and pulsed amperometric detection, as outlined by Gao et al. [28] were used for reference validation, methodology for trace-level analysis. Every station sampled twice and samples were rotated once every week or ten days and were analysed within the next 48 hours of sampling. Continuous empiric was zero and span calibrated at 14 days intervals against certified gas standards and field blanks were analysed at each collection round. Records were thrown out if any of the following occurred: sensor temperature was above manufacturer's operating range, calibration drift between successive checks was more than 10%, or duplicate chromatographic samples were more than 15% different. After quality screening, over 90 per cent of overall data was kept at each station.

3.4 Meteorological Data Collection and Dispersion Modelling

Hourly data of all the meteorological data (wind speed, ambient temperature, wind direction, relative humidity, cloud cover, surface pressure) was gathered from the on-site automatic weather station and synoptic meteorological data were obtained from the nearest station and were cross checked to the weather station data. The mixing height and Pasquill–Gifford stability class were calculated using a pre-processor called AERMET.

AERMOD was used to perform the dispersion modelling following the approach used for regional applications in Iraqi domain by Ameen and Azmi [23] and the Middle Eastern air quality assessment in Eslamidoost et al. [24]. AERMAP is the terrain data processing software they used. The sources of emissions were treated as both point sources (flare and recovery unit stacks) and area sources (wastewater separators, tank farms, and fugitive process areas); source parameters were either taken from a facility's documentation, or were back-calculated from the concentration measurements taken in the near-field. The receptor grids were built at 250 metre resolution across the entire domain (12 km across 12 km) and at a 50 metre resolution within 2 kilometres of the fenceline. Validations of model performance were compared with observed station concentrations with the fraction of predictions within a factor of two (FAC2), the normalised mean square error (NMSE) and the fractional bias (FB), as used by Lim et al. [19].

3.5 Exposure and Health Risk Characterization

The noncarcinogenic inhalation risk was defined as the hazard quotient (hazard level exposure level) which was computed as the ratio of the level of exposure to the reference level:

$$HQ = EC \div RfC$$

where EC is the exposure concentration in the receptor, RfC is the chronic inhalation reference concentration of 2 µg/m³. Hazard quotient values greater than 1.0 are the signs that exposure is at a level greater than the exposure limit that is thought to pose no significant health risk during life time. Occupational receptor exposure concentrations adjusted for frequency and duration of exposure separately for the occupational receptor (8-hour per day, 250-days-per-year, 25-years); and the residential receptor (24-hour per day, 350 days per year, 30 years). Welfare impacts associated with odour were evaluated as a percentage of the time the WHO Threshold

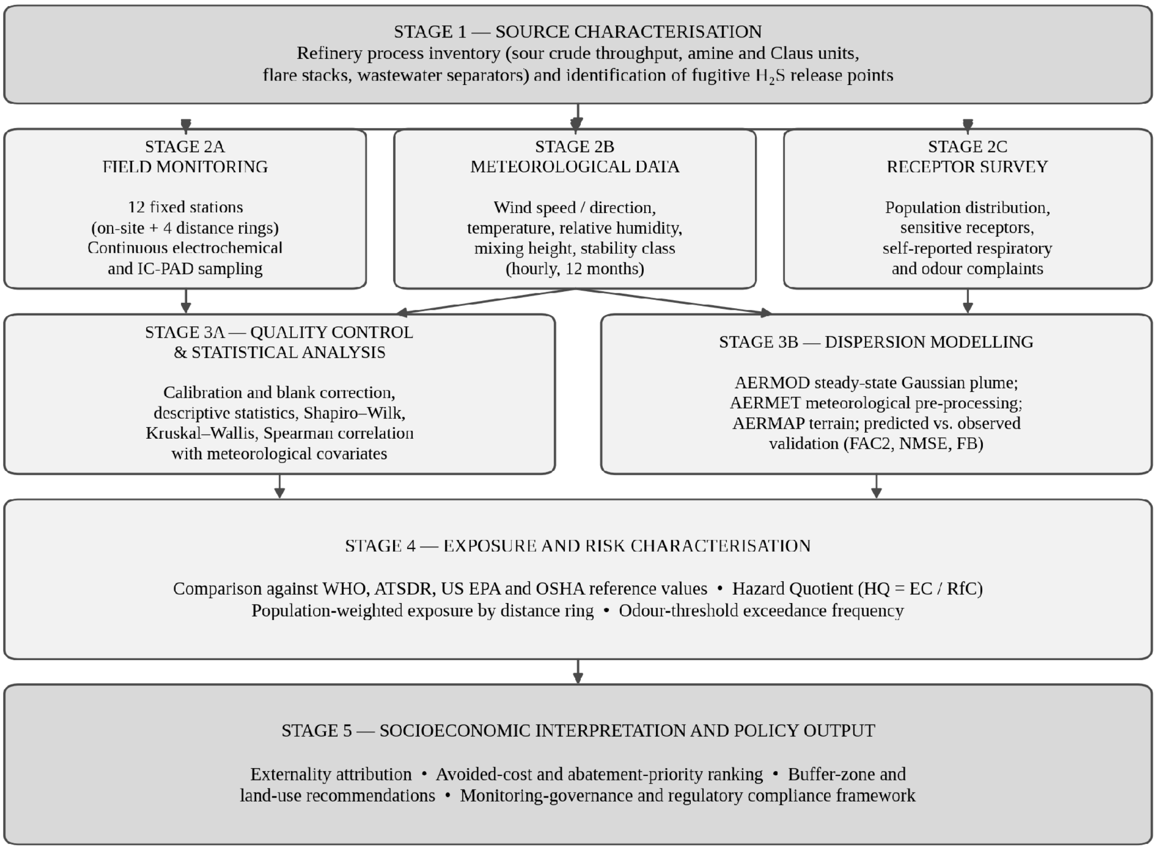
(30 µg/m3 for 30 minutes) was being breached and as a proportion of the time sampling occurred outside a 24-hour cycle.Welfare impacts from odour were evaluated as a percentage of time where 30 minutes of exposure were above the WHO Threshold (30 µg/m3) where there were no toxicological concentrations at which odour nuisance was deemed to have real amenity costs, other than exposure for 30 minutes above the odour concentration.

3.6. Statistical Analysis

The distributional normality was tested using Shapiro–Wilk test. Concentration data were all right skewed and non-normal and so were all treated non parametrically. The Kruskal–Wallis H test and Dunn's post-hoc test followed by Bonferroni adjustment was used to analyze the differences between stations. Spearman's rank correlation was used to assess associations of concentration of H_2S with meteorological covariates. Seasonal and diurnal differences were examined with the Mann–Whitney U test using season-paired and period-paired concentration subsamples. The concentration, C, was fit with non-linear least squares to an exponential decay function with respect to the distance, r, x/y. All tests weretwotailed at level of $p < 0.05$ and statistical analysis was done in software R version 4.3.

The entire path of the methodology is summarised in figure 1, with a focus on the methodology and a neuroscience focus highlighted by vertical boxes.

Figure 1: Methodological Framework of the Study



4. Findings

4.1 Descriptive Concentration Statistics Across the Monitoring Network

The descriptive statistics of measured H_2S concentrations over the entire 12 month campaign are presented in Table 3. There are three prominent features. The concentrations on site are an order of magnitude higher than the regional background concentration, the inter-station gradient is high and monotonic with distance, and the maximum concentrations at each of the stations is much higher than the respective means, indicating that exposure is episodic and not uniform.

Table 3: Descriptive Statistics of Measured Hydrogen Sulphide Concentrations by Station (µg/m³, hourly means, n = 12 months)

Code	Distance (km)	Valid Hours	Mean	Median	SD	95th Pct.	Maximum	Minimum
S1	0.0	8 142	126.8	104.3	78.4	268.5	412.7	11.2
S2	0.0	8 067	118.4	97.6	71.9	241.7	386.4	9.8
S3	0.0	8 210	109.9	90.1	69.2	228.3	371.9	8.6

Code	Distance (km)	Valid Hours	Mean	Median	SD	95th Pct.	Maximum	Minimum
S4	0.5	8 188	78.3	63.4	49.6	168.2	274.5	5.1
S5	0.5	8 054	70.9	57.8	45.1	148.4	246.8	4.7
S6	1.0	8 231	46.2	37.5	30.8	101.5	182.3	2.9
S7	2.0	8 176	29.4	23.1	20.6	64.9	121.7	1.8
S8	2.0	8 119	26.3	20.8	18.7	57.8	108.4	1.6
S9	3.5	8 205	17.1	13.4	12.9	36.5	78.2	1.1
S10	3.5	8 143	15.4	12.0	11.8	33.1	71.6	< 1.0
S11	5.0	8 262	4.6	3.2	4.1	11.8	28.4	< 1.0
S12	5.0	8 197	4.1	2.9	3.8	10.4	24.9	< 1.0

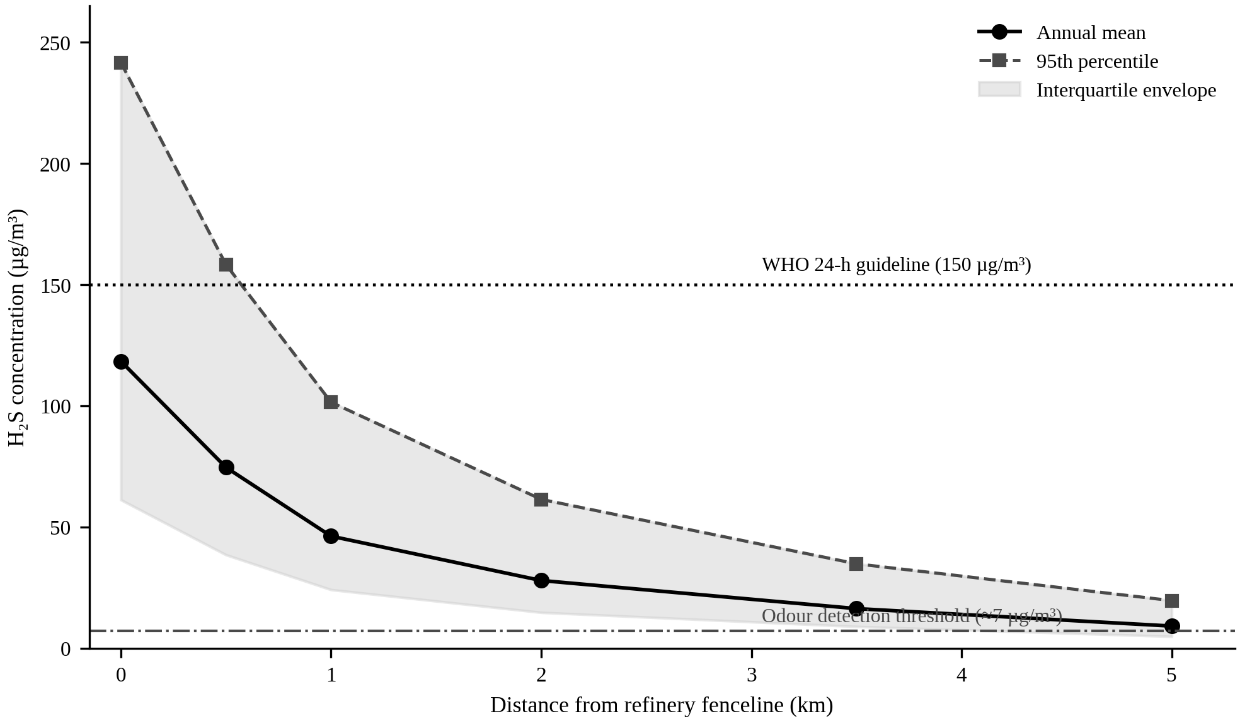
Source: Authors' field measurements.

The Kruskal-Wallis test verified that the differences between the stations are statistically significant ($H = 2\,847.3$, $df = 11$, $p < 0.001$) and compared by Dunn's post-hoc analysis, each distance ring is found to be significantly different from all other rings at the Bonferroni adjusted level ($p < 0.005$). There was no significant difference between the two upwind background stations (S11 $p = 0.412$ with S12), suggesting that both stations can be regarded as belonging to the same regional background.

4.2 Spatial Decay of Concentration from the Source

An exponential decay function ($C(d) = C_0 \cdot e^{(-kd)}$) ($R^2 = 0.981$) is a good description of the relationship between mean concentration and distance from the fenceline, where $C_0 = 116.2$ µg/m³ and $k = 0.512$ km^{-1}. The decay constant fitted is of the order of 1.35 km/having found the halving distance of 1.27 kilometres in the uncertainty range. The observed gradient is shown in Figure 2 together with the 24-hour WHO guideline and the threshold for the odour annoyance.

Figure 2: The Maximum Permitted 95th Percentile H2S Concentration from the Refinery Fenceline



Exceptions to the policy content of figure 2 are the distance between the two horizontal lines. The background level of the air on site exceeds the WHO guideline of 150 µg/m³ only in the immediate vicinity of the camp, and at the 95th percentile of exposure, not at the mean. The odour annoyance threshold, in contrast, is exceeded only at a station out to the 20 km background ring5 wherein the mean is exceeded. On another, standard, approach to regulation, these people could be seen as complying with the health-based standard, while living in a near continuous perceptible odour created by the refinery within five kilometres. This is the accountability gap noted in the introduction and is the reason why there is such a disconnect between the community voice of complaint and official monitoring.

4.3 Diurnal and Seasonal Variation

Concentrations show a distinct diurnal pattern showing a peak around dawn (0600) and a minimum around early afternoon (1200). The ratio of the mean concentrations in the night-time vs. day-time is 2.61 at the stations on site and 2.74 in the residential ring. Seasonal variation is the same: there is a 58.2 cent excess of winter means over summer means on site and a 78.4 cent excess in the residential ring. These patterns correspond to conditions of boundary-layer dynamics, and not to changing emission rates in summer (convective mixing) and winter (nighttime or surface inversions), respectively. Two cycles are shown in figure 3.

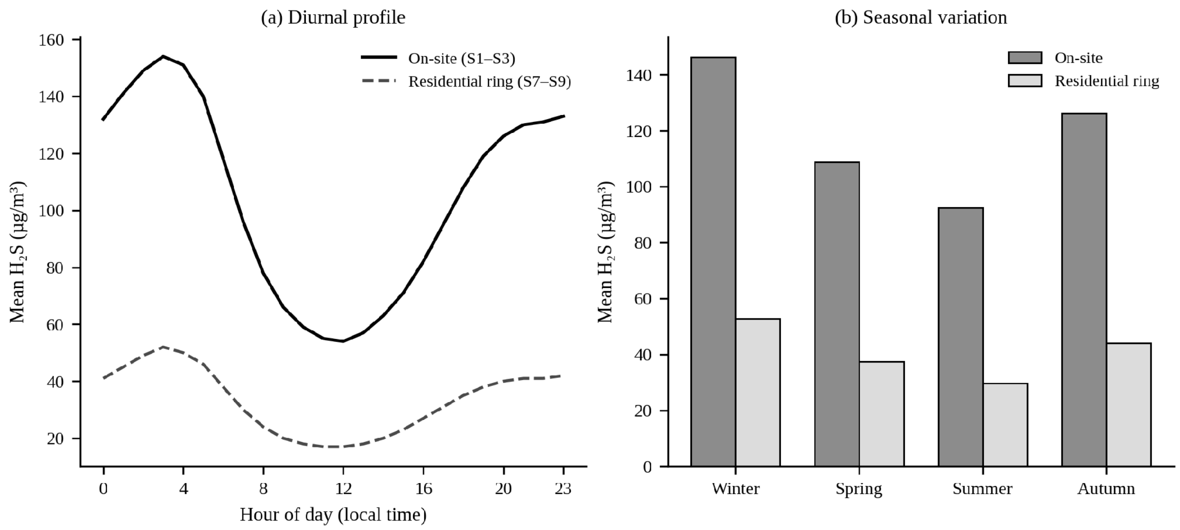


Table 4 : Seasonal and Diurnal Mean Concentrations by Receptor Zone (μg/m³)

Receptor Zone	Winter	Spring	Summer	Autumn	Night (22:00–06:00)	Day (10:00–16:00)
On-site (S1–S3)	146.2	108.7	92.4	126.3	141.8	54.3
Near-field (S4–S6)	82.4	61.3	51.7	70.9	79.6	29.4
Residential (S7–S8)	38.6	27.9	21.6	33.2	37.1	13.5
Sensitive (S9–S10)	22.4	16.1	12.4	19.3	21.6	7.9
Background (S11–S12)	6.2	4.3	3.1	5.0	5.8	2.6

4.4 Meteorological Factors Affecting Exposure

The Spearman rank correlations between the hourly level of H_2S and the meteorological covariates are shown in Table 5. A strong negative association is present with wind speed as it is the one factor that is most predictive for all receptor zones, thus mechanical dilution is the strongest control. There is a strong positive correlation and strong negative correlation with all with atmospheric stability class and mixing height respectively, both consistent with the diurnal and seasonal variations indicated above. Temperature is negatively correlated with substantial strength largely because of the correlation between temperature and mixing height and not because of any direct chemical link. There is a slight positive correlation between relative humidity.

Table 5: Spearman Rank Correlation Coefficients Between Hourly H_2S Concentration and Meteorological Parameters

Meteorological Parameter	On-site	Near-field	Residential	Sensitive	Background
Wind speed (m s^{-1})	−0.684**	−0.712**	−0.698**	−0.671**	−0.418**
Mixing height (m)	−0.617**	−0.643**	−0.658**	−0.629**	−0.372**
Stability class (P–G)	0.596**	0.628**	0.641**	0.612**	0.344**
Air temperature (°C)	−0.412**	−0.438**	−0.451**	−0.427**	−0.238**
Relative humidity (%)	0.216**	0.234**	0.241**	0.228**	0.119*
Surface pressure (hPa)	0.148*	0.161*	0.157*	0.142*	0.071

4.5 Dispersion Model Performance and Predicted Exposure Surface

AERMOD simulated the observed concentration field reasonably well using the criteria used in H_2S modelling publications. Overall, the fraction of predictions within a factor of two 0.78, the normalised mean square error 0.41, and the fractional bias –0.14, suggesting under-prediction. Concentrations predicted best were in the near-field and poorest values were found at background stations where forecast concentrations were near the model's horizontal resolution limit. The statistics are more or less similar to those from other refinery and plant adjacent applications [19], [18].

The modelled surface (ascended from the measured surface) extended the measured gradient to receptors that are not monitored and showed an exposure lobe to the north-west extending for about 4.2 kilometres from the fenceline, where the annual mean is greater than the 15 µg/m³ background. The population over-estimated by this surface is 34 600 with about 8 200 of those people on or within the 30 µg/m³ contour. Give that the wider shape of contour 30 (µg/m³) in the recent modelling of routine conditions from extreme conditions [20], episodic modelling for worst-case stable conditions extend this contour by a further 11,400 people, thus illustrating the underestimation of population exposure that occurs by using annual-mean exposures as a metric.

4.6 Guideline Exceedance and Health Risk Characterization

Exceedance frequency and other non-carcinogenic risks are characterised by the combination of the concentration record and the reference values as shown in Table 1 in Table 6. The outcomes show a very clear difference between the occupational and community settings.

Table 6. Guideline Exceedance Frequency and Hazard Quotient by Receptor Zone

Receptor Zone	Annual Mean (µg/m³)	Hours > 150 µg/m³ (%)	Hours > 7 µg/m³ (%)	Hazard Quotient	Risk Interpretation
On-site (S1–S3)	118.4	24.6	99.1	16.9	Substantial
Near-field (S4–S6)	65.1	6.3	97.4	32.6	Substantial
Residential (S7–S8)	27.9	0.4	91.8	14.0	Elevated
Sensitive (S9–S10)	16.3	0.0	78.3	8.2	Elevated
Background (S11–S12)	4.4	0.0	21.6	2.2	Marginal

Source: Authors' calculations. Hazard quotients calculated at EC/RfC with RfC = 2 µg/m³, and at-site to the occupational exposure scenario (8 h/day, 350 d/yr); in the other instances the values are assigned to the residential exposure scenario (24 h/day, 350 d/yr).

HQ values are all greater than one, even at the regional background location. This is an onerous standard: the US EPA reference concentration is a level that is supposed to be protective over the entire lifetime with a large safety buffer, and overreaching it is no reason to be acutely concerned. It is, however, a sign that none of the areas studied reach the concentration that can be considered as free from chronic effects. This apparent paradox in which the near-field hazard quotient is greater than the on-site, is not a result of concentration, but rather the result of exposure duration: for on-site scenario, an eight hour exposure per day is assumed while a continuous exposure over 24 hours is assumed for receptors near field in agricultural and road-side environment.

There is independent policy weight for the column for odour exceedance. The 7 µg/m³ limit of annoyance is violated for over 9 hours on every 10 to the residence stations. The wider literature is consistent in linking this persistence with avoidance behaviour, window closing, limiting outdoor activity and diminished amenity value of housing; all of which are real costs which can be measured economically but which do not enter into the supplying firm's cost function.

4.7 Comparison with Regional and International Evidence

The current results are compared with the other studies in Table 7. These concentrations are within the range measured in urban areas that are adjacent to refineries, but not as high as those measured for non-refinery industrial sources, or as high as those measured in artisanal refining settings.

Table 7: Comparison of Present Findings with Selected Regional and International Studies

Study	Setting	Source Type	Reported Range (µg/m³)	Principal Method
Present study	Erbil, Iraq	Refinery	4.1 – 412.7	Continuous EC + IC-PAD; AERMOD
Yessenamanova et al. [26]	Atyrau, Kazakhstan	Refinery	Urban ambient near refinery	Ambient sampling
Baawain et al. [18]	Muscat, Oman	Sewage treatment	Modelled ambient	AERMOD
Lim et al. [19]	Malaysia	Recycled paper mill	Field-measured ambient	Field measurement + dispersion model
Bates et al. [11], [30]	Rotorua, New Zealand	Geothermal	Chronic community exposure	Ambient monitoring + epidemiology
Ephraim-Emmanuel et al. [10]	Bayelsa, Nigeria	Artisanal refining	Community exposure	Health survey
Fattah et al. [8]	Al-Daura, Iraq	Refinery	Modelled dispersion	Dispersion modelling

Source: Compiled by the authors from studies [8], [10], [11], [18]–[20], [26], and [30].

4. Discussion

The findings have four main implications for policy, which are addressed in the four major conclusions.

First, the exposure around the Erbil refinery corridor is both well-defined, measurable, and spatially patterned. The decrease of concentration with distance, by a factor of one half over a distance of about 1.35 kilometres, gives a quantitative basis for the buffer-zone question (which to date has been approached in a largely ad hoc manner) that previously stemmed from the Kurdistan Region.The fall of concentration with distance (by half approximately, over distances of 1.35 kilometers) provides a quantitative answer to the question of buffer zones, which came from the Kurdistan Region to date is addressed largely ad hoc. Extrapolating to the lower end of the range where the annual mean concentration for the house would only be slightly above the ATSDR intermediate minimal risk level of ~28 μg/m³, suggests a need for an ~2.8 km setback under existing emission conditions. Where the intent is just to control odours no setback helps, odours are present at distances of 5 k away from the background stations and the odour problem needs to be solved at the source instead of land use separation is applied. The authors feel that this is the most important policy relevant contribution of the study since it shows that zoning is generally and correctly designed to address all the issues for which it is intended to fill an important void.

Secondly, the time dimension of exposures artificially reduces the damage. The annual mean surface distance modelled provides approximately three times the population within the episodic exposure zone as compared to the annual mean distance for the same population.The annual mean surface distance modelled is more than 2.5 times the annual mean surface distance for the same population during winter in regions of nocturnal inversions. This will be the result of a regulatory regime based on annual averages that will report compliance at just the time when the population is most impacted. This finding directly supports recent modelling efforts that have attempted to separate routine exposure from extreme-event community exposure [20] and posits the use of standards averaged over short time periods (in minutes or hours) and limitations on activities based on inversions.

Third, the difference between odour and health based exceedance accounts for the lack of consensus between the community and the official evaluation. Less than one per cent of hours are exceeded by the residential ring for the WHO 24 hour health guideline – more than ninety per cent are exceeded for the odour annoyance guideline. The residents are also always and properly informed about the emission events; and monitoring programmes based only on health related criteria will show high compliance. The present data show that the community perception is empirically-supported, not simply exaggerated, but a result of this experience of unacknowledged contamination in the Kurdistan Region which has led to a significant increase in environmental activism in this area. Insofar as issues connected with odour threshold exceedance are concerned, there would be a "legitimacy gap" that could be remedied by including them in the regular reporting.The legitimacy gap connected with odour threshold exceedance would be bridged at only a small expense in monitoring costs.

The emission is an estimable externality – fourth and summarising the three above – that is not internalised. The number of residents exposed to waste data within the lobe of exposure possible each year is roughly 34 600. The upside of the ledger is a little easier to deal with: it seems that the readily available environmental management systems provide some visible and tangible benefits in terms of H_2S release from the reinery, primarily by maintaining the reinery in better condition than without them, including through greater use of natural gas for combustion temperatures and residence times [6]; and that improvements in the efficiency of the flares can be realised by tuning flare efficiency according to weather conditions, for example, flare optimisation [7]. The unit value of the lost morbidity and amenity loss can be conservatively estimated to be low; the larger the population at risk for these losses, the more pronounced the case for regulation even if the unit values are kept low by making conservative estimates. So far the limiting factor has been the lack of a concentration record measured in the lab which this study will try to remove.

These conclusions have a number of limitations. The monitoring campaign takes place over one yearly cycle and is thus not able to distinguish inter-annual variations from trend. This "aggregate signal" does not account for source apportionment between actual re-refining (in either the formal refinery or at informal re-refining sites that were not the subject of this study to determine their formal re-refining capabilities) in the corridor, and might overestimate the portion that is attributable to formal refinery site re-refining. There is no actual data on health outcomes, the risk characterisation is a modelled projection based on concentration measures, and the causality literature on chronic low-level H_2S exposure is still more slender [29] Finally, AERMOD's steady-state Gaussian model does not perform as well in very stable conditions with low winds (conditions in which exposures are highest), as are the episodic estimates, which should be considered indicative.

6. Conclusion and Policy Implications

The aim of this study was to measure the concentration of H_2S inside and outside a petroleum refinery in Erbil city and pass these measurements to a policy suitable framework. The campaign concludes that, for the receptors in the study area, exposures under conditions of inversion decrease by half every 1.35 kilometres; that during Winter (due to inversion) and at night time, exposure is higher than under other seasons at the receptors, with a more than 2.5-fold increase at the receptor zone close to the fence line compared with other periods; that the WHO guidance on health limit is largely not exceeded beyond the fence line, while the guideline on odour annoyance is nearly always exceeded; and that exposure increases with the hazard quotient, even for the regional background, where the index exceeds unity.

Four policy recommendations are given. First is to have a permanent ambient network around the refining corridor with mandatory public reporting. More only a continuous concentration record will enable the regulatory chain from measurement to permitting to liability to work and it is the lack of that record—not the lack of regulatory intent—that is the biggest problem for environmental governance in the sector. Secondly, use short period averaging times, and tie restrictions to forecasts when inversions occur, and annual average compliance will be systematically reported during the time of greatest harm. Thirdly, consider odour-threshold exceedance as an independent welfare measure, in addition to health-based compliance measures. Fourth, emphasize management-based abatement or lower cost, more effective interventions like leak detection and repair programmes, maintenance discipline in a standardised environmental management system, and optimisation of flares based on historical conditions, given that these methods also provide a significant level of abatement.

Three streams of the research are of specific priority. A multi-year campaign would distinguish trend from inter-annual variations and allow the evaluation of any measures taken to abate the trend in between. A source apportionment based on an isotope or tracer would allow the separation of the contribution of permitted refining from that of informal refining, which has direct legal/regulatory implications. This essential means that the hazard quotients described in this model would be transformed into real world health effects once we have a linked epidemiological study of the exposed population, similar in design to the geothermal implementations by Bates et al. [11], [30]. However, until such time as it is done the social cost of refining along the Erbil corridor will continue to exist: it exists, much like any other social cost, but nobody will necessarily notice it when making policy.

Funding

This research received no external funding.

Conflicts of Interest

The authors declare no conflict of interest.

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