ARID TECHNOLOGIES INC.

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28 September 2004

Mr. Thomas A Driscoll
Senior Environmental Scientist
United States EPA
Office of Air Quality Planning & Standards
Emissions Monitoring and Analysis Division
Emissions Factors and Policy Applications Group (D243-02)
109 T.W. Alexander Drive
Research Triangle Park, North Carolina 27709

Dear Mr. Driscoll,

As a follow-up to my presentation on 20 September at the Public Meeting hosted by USEPA, I am pleased to provide my written statements and supporting information concerning Stage II VRS and ORVR incompatibility.

Background

ARID Technologies, Inc. has been directly involved in gasoline vapor recovery technology and associated storage tank dynamics since the company was founded in 1993. From inception to present, ARID has installed more than 125 PERMEATOR systems worldwide, and our experience includes system installations and technical studies conducted in Japan, Europe, South Korea, Mexico and the United States. ARID has developed an Evaporative Loss Model which is used to quantify "incompatibility excess emissions" at a given refueling facility based on five primary factors: gasoline RVP, gasoline storage tank temperature, V/L ratio of the Stage II system, altitude, and ORVR vehicle population. This model has been shown to provide very accurate results between measured and modeled values throughout a diverse range of parameters compiled from refueling facilities located around the world.

Widespread Use

It appears as though stakeholders are interested in the concept of "widespread use" due to the assumption that as more and more vehicles are equipped with ORVR controls, the need for Stage II vehicle vapor recovery systems will diminish. The further assumption made in the Issue Paper is that the combination of Stage II and ORVR technologies yields lower overall emissions than the emissions generated with either technology used alone[1].

ARID respectfully challenges the latter assumption, as our measured and modeled data show a remarkable increase in the incompatibility excess emissions (IEE) generated in the storage tank system as a result of the fundamental incompatibility of Stage II vacuum assist and ORVR technologies. In Appendix 1, Figures 1-4 show the In-use Control Efficiency (IUE) and overall

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[1] Stage II Vapor Recovery Systems Issues Paper, Thomas Driscoll, August 12, 2004, pages 17 and 21

storage tank evaporative and vehicle refueling emissions at an individual gasoline dispensing facility. The dispensing facility conditions are as follows:

- Δ Throughput: 330,000 gallons per month in 2005 (growth rate of 2.5% per year, thereafter)
- Δ V/L = 1.05 (Stage II vacuum assist system, ORVR penetration per CARB)
- Δ Altitude: 1,000 feet above sea level

Two cases are presented: Figures 1 & 2 are based on 13 RVP fuel at 72 F (Case 1), and Figures 3 & 4 are based on 9 RVP fuel at 85 F (Case 2). Case 1 represents a moderate climate USA site in the winter months, and Case 2 represents a typical moderate climate USA site in the summer months. As seen in Figure 2, with ORVR and Stage II systems employed, year 2005 storage tank and vehicle refueling emissions equal 30 tons per year for a single refueling station (0.24% of throughput = 15 lbm/1,000 gallons). As ORVR penetration and fuel consumption increase in the future years, the emissions reach a level of 40 tons per year by 2010 (0.29% of throughput = 20 lbm/1,000 gallons). The year 2005 and 2010 IEE emissions exceed the AP-42 figure of 1 lbm/1,000 gallons by a factor of 15 and 20, respectively.

In Figure 1, the In-use Control Efficiency (IUE) for the ORVR and Stage II system combination begins at about 50% in year 2005. In future years, the overall recovery efficiency for this option declines and approaches the ORVR only option. Unfortunately, the options are converging at an IUE of about 30% (The best achievable IUE by ORVR only is approximately 50%). Conversely, the ORVR and APCD option begins with an IUE of about 80% and approaches a level of about 98%.

Case 2 plots are presented in Figures 3 & 4. As seen in Figure 4, with the ORVR and Stage II systems in use, year 2005 storage tank and vehicle refueling emissions equal about 18 tons per year, and the emissions increase to a level of about 22 tons per year by 2010. In Figure 3, the In-use Control Efficiency (IUE) for the ORVR and Stage II system option begins at about 60% in year 2005. Again, the ORVR only option and the Stage II/ORVR option converge to a low IUE – in this case about 40%. The ORVR and APCD option begins with an IUE of about 76% and approaches a level of 98%.

For comparison, the measured IEE for two sites are presented in Appendix 2. One site is located in Grass Valley California and the other site is located in Lantana, Florida. As seen in the data summary, the California site IEE measure approximately 0.34% of throughput and the Florida site IEE average about 0.36% of throughput. The excess vapor generation rate is very accurately calculated, and the hydrocarbon concentration of the vapors generated was estimated. The accurate quantification of the IEE is readily accomplished by application of known test methods, and ARID strongly recommends that such testing is conducted and/or supervised by USEPA.

For yet another comparison, additional data are presented for each site in Appendix 3. The measured savings in evaporative losses (IEE) are shown to be 0.40% of throughput and 0.37% of throughput for the California and Florida sites, respectively. These data were generated with the use of ARID's remote data monitoring and acquisition technology used in conjunction with sensors installed on the PERMEATOR (Please recall the details of these calculations presented to you and USEPA Staff during our previous meeting in August 2004).

In general, ARID would like to emphasize the presence and magnitude of the incompatibility excess emissions, IEE. Instead of considering such emissions as part of ancillary issues, ARID feels that the magnitude of these emissions are such that they must strongly influence the thought processes contemplated for the definition and supporting algorithms related to "widespread use". In addition, these emissions must be considered in the context of the administration of potential SIP credits for various aspects of vapor recovery.

Emission Factors for Fugitive Emissions

With reference to the plot presented in Appendix 4, Mr. Paul Marzilli of the California Air Resources Board (CARB), calculated fugitive emissions with PERMEATOR "OFF" and with PERMEATOR "ON" at ARID's Grass Valley Chevron test site located in Grass Valley California[2]. The results of these measurements are as follows:

	PERMEATOR "ON"	PERMEATOR "OFF"
UST average pressure	0.178 inches H_2O	2.823 inches H_2O
Fugitive emission factor	0.074 lbm/1,000 gallons	0.782 lbm/1,000 gallons

The ratio of the fugitive emission factor with PERMEATOR OFF to PERMEATOR ON is equal to .782 /.074 = 10.6: 1. In addition, the ratio of the fugitive emission factor with PERMEATOR ON to the IEE factor calculated in Case 1 (2005) is 15 /.074 = 202.7. Thus, the UST vent emissions exceed the fugitive emissions by more than 200 times.

The accounting of the emissions as either "fugitive" or "vent emissions" is largely an academic exercise. The key concept is that an excess vapor generation rate is present within the storage tank system (We use the term "vent emissions" to include emptying, breathing, and IEE emissions). This excess vapor volume created will result in an observed pressure increase within the storage tank system. A relatively "tighter system" will yield higher vent emissions and a relatively "leaky system" will yield higher fugitive emissions. In general, if an APCD device is employed to reduce the overall storage tank pressure while at the same time capturing and recovering vent emissions, the driving force for fugitive emissions is dramatically reduced, and the vent emissions themselves are significantly reduced.

When one combines the Bernoulli equation with the Continuity equation, one obtains the following expression for relating the mass of emissions through a hole in a pressurized system:

m = A x (2 x P atm/RT x (P tank – P atm)) ^1/2; where

m = mass flux
A = effective area of the "hole" or "holes" in the system
P atm = atmospheric pressure
R, T = ideal gas constants
P tank = tank pressure

Thus, the square root of a pressure differential accurately describes the variation of fugitive emissions with pressure for a given temperature and hole size.

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[2] Email correspondence from Mr. Marzilli to Ted Tiberi, ARID Technologies, Inc., Wednesday, April 21, 2004, cc: Cindy Castronovo and Laura McKinney (CARB). Method used was TP-201.2F.

Another point is that the API and CARB estimated incompatibility excess emissions are on the same order of magnitude as the fugitive emissions measured with PERMEATOR OFF. More importantly though, the magnitudes of these IEE are very small in comparison to the Case 1 vent emissions reported by ARID.

	API, 2004 Study	**CARB, 1999 Study**	**ARID, Case 1**
IEE[3]	0.33 lbm/1,000 gal	0.86 lbm/1,000 gal	15 lbm/1,000 gal

The ratio of each value to that reported by ARID is 45:1 and 17:1, for the API and CARB figures, respectively.

SIP Credits

After proper quantification of IEE, decisions on providing SIP, or other market based emissions reduction credits can be properly formulated. From Figures 1 & 3 in Appendix 1, one can quickly see that the maximum recovery efficiency is provided by the integration of ORVR, Stage II and APCD control technologies. The second best option, with significantly reduced cost of ownership (and operation) is the combination of ORVR and APCD control technologies. Assuming the ultimate objective is cleaner air, USEPA and individual states can craft various innovative strategies which allow gasoline dispensing facility owners/operators to proactively take steps to significantly reduce emissions of VOC (volatile organic compounds) and HAPS (hazardous air pollutants). In addition to enjoying the economic benefits of being able to resell the same volume of fuel which they purchased, gasoline marketers will appreciate the cleaner environment in close proximity to their refueling station. As an added bonus, any SIP or emission reduction credits accruing to the state and/or gasoline marketer can accelerate adoption of APCD technologies.

The “Issue Paper” asks for comments about encouraging increased inspection and maintenance of hardware employed at gasoline dispensing facilities. ARID feels that in the past, the incentive for “good housekeeping” practices by facility owners has not been present. The two primary reasons for this are 1.) If a station owner put forth the effort to ensure leak integrity and proper operation of their vapor recovery system, they could guarantee themselves that all their lost product would escape their storage tank system through the p/v vent, and 2.) The sole reliance on centralized monitoring of tank levels and liquid line leak test results removed the involvement of the local site personnel.

These negative factors can be mitigated by the following developments: 1.) The use of an APCD now gives the station owner the proper incentive to ensure hardware is properly maintained and that the vapor carrying components remain leak-tight. Instead of losing vapors at the UST vent (or fugitive sources), the wise station owner will diligently maintain their APCD equipment with the confidence that their efforts and investment will be rewarded with saved product. 2.) The use of simple monitoring technology (such as overall storage tank pressure and APCD run times) can be coupled with local involvement of station personnel. For example, visual inspections may be helpful in identifying catastrophic liquid leaks, but visual inspections are perhaps not as insightful for identifying vapor leaks or vacuum pump degradation within sealed housings. As a solution, consider the impact of continuous monitoring of storage tank pressure from a central

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[3] Table 1, page 14, Stage II Vapor Recovery Systems Issues Paper, Thomas Driscoll, August 12, 2004

location, with exceptions reporting capability. This means that if storage tank pressures (or APCD duty cycle) varied significantly from the "normal profile" expected, the system would alert site personnel to conduct further inspections. The site personnel assigned by the marketer (for the individual station, or group of stations) would then further investigate typical leak sources and would arrange for detailed hardware inspections (vacuum pump service) or a leak decay test, if necessary, to pinpoint the anomaly.

This approach re-involves the local personnel to take "ownership" of the inspection and maintenance processes. Due to the use of an APCD, their efforts are rewarded with saved product. It seems reasonable that SIP credits (or other market based credits) could be linked to the use of APCD systems, integrated monitoring and local inspection/maintenance programs to further accelerate adoption of good housekeeping practices. In addition, the designation of BACT, MACT or RACT for the use of APCD technology and/or inspection & maintenance programs could possibly trigger additional SIP credits, government subsidies, tax relief or market based emission credits.

Monitoring of Stage II

The issue paper raises an interesting point regarding the capital investment to monitor systems which are likely being phased out. ARID believes that useful monitoring information can be obtained from "macro" variables such as combined storage tank pressures and APCD run times. The use of "micro" variables (A/L ratios) generated at individual refueling points with so-called ISD systems does not seem necessary nor prudent, considering the cost of the information generated coupled with the likelihood of a short useful lifetime of such equipment. On the other hand, the need for "back-end" APCD technology will continue in perpetuity, regardless of the "front-end" mix of Stage II vacuum assist and ORVR technologies. Thus, a monitoring approach of macro variables associated with operation of APCD technology represents a simple, elegant, robust and much more long-term and cost effective option for petroleum marketers.

Conclusion

ARID strongly supports the need for field testing to accurately quantify the storage tank vent emissions (IEE, emptying and breathing and fugitive). We support further emissions factor work on items (a) – (c) listed on page 28 of the "Issues Paper". New, updated emissions factors are needed to allow relevant decisions to be made regarding widespread use and the potential administration of SIP and other market based credits. ARID also believes that a need exists for APCD technology now and in the future, regardless of the mix of Stage II and ORVR technologies used for vehicle vapor recovery. The APCD technology can be considered "Stage III" technology – storage tank vapor containment technology as opposed to vehicle vapor collection equipment.

The stakes in this discussion are high, as VOC's and HAPS are being emitted in great quantities and in close proximity to gasoline dispensing facilities. Often times, these refueling facilities are located relatively close to large population centers. In recent years, the concept of "co-branded" sites has resulted in consumers and facility employees spending much more time within the refueling station environment. This extra time spent directly correlates to increased exposure to potentially harmful emissions. As seen in Appendix 5, recent studies have quantified the increased emissions and their associated impact on human health.

Thank you for the opportunity to provide our comments and data. We are available at the convenience of USEPA Staff to discuss in-person in Research Triangle Park, via email, or by telephone any of the information presented in this correspondence. ARID looks forward to helping USEPA understand, measure and mitigate gasoline storage tank evaporative losses.

Sincerely,

Tedmund P. Tiberi

Tedmund P. Tiberi
President

Appendix 1
Storage Tank & Vehicle Refueling Emissions
In-use Control Efficiency (IUE)

Figure 1: In-use Control Efficiency (IUE)

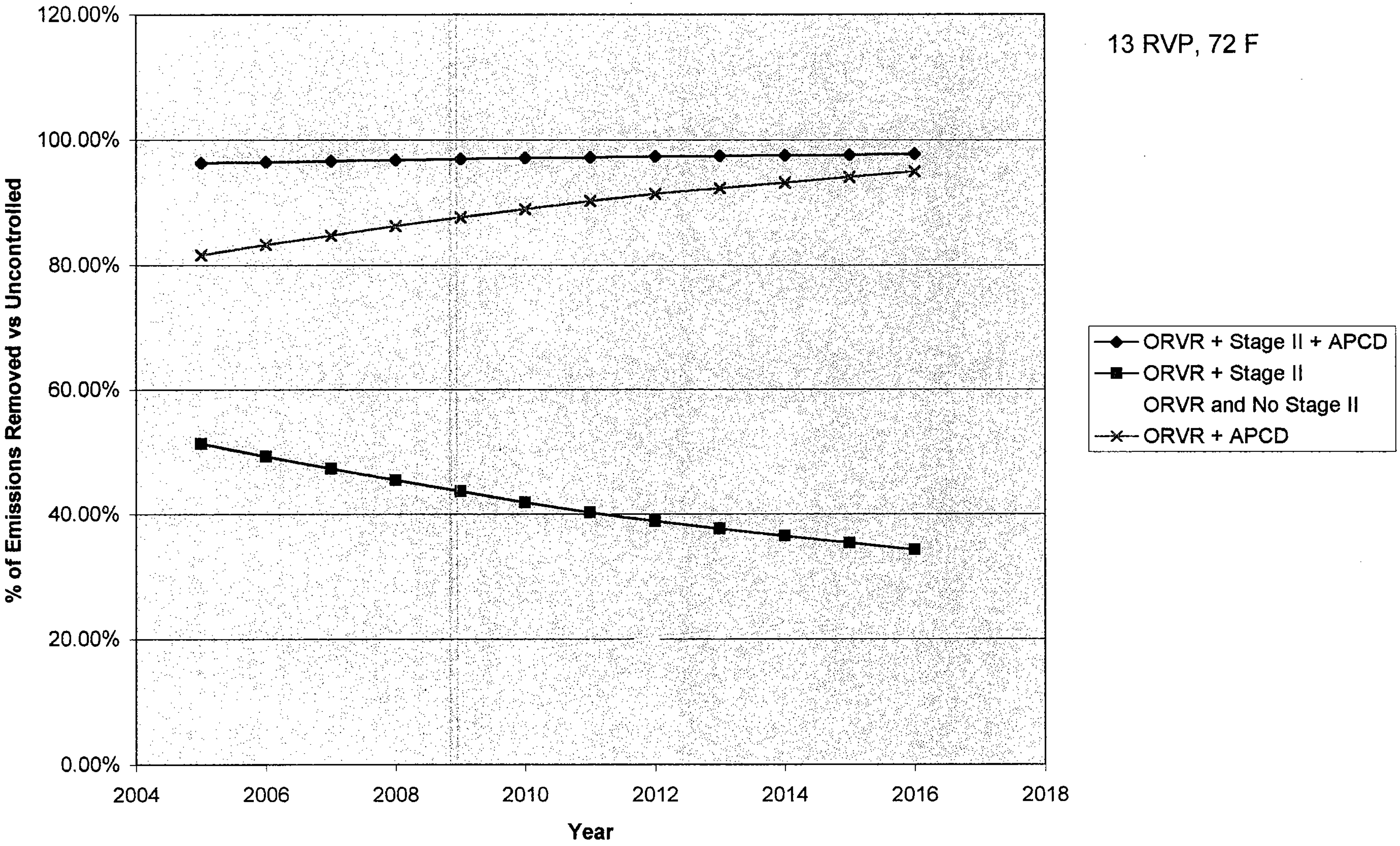


Figure 2: Storage Tank Evaporative and Vehicle Refueling Emissions at a Gasoline Dispensing Facility

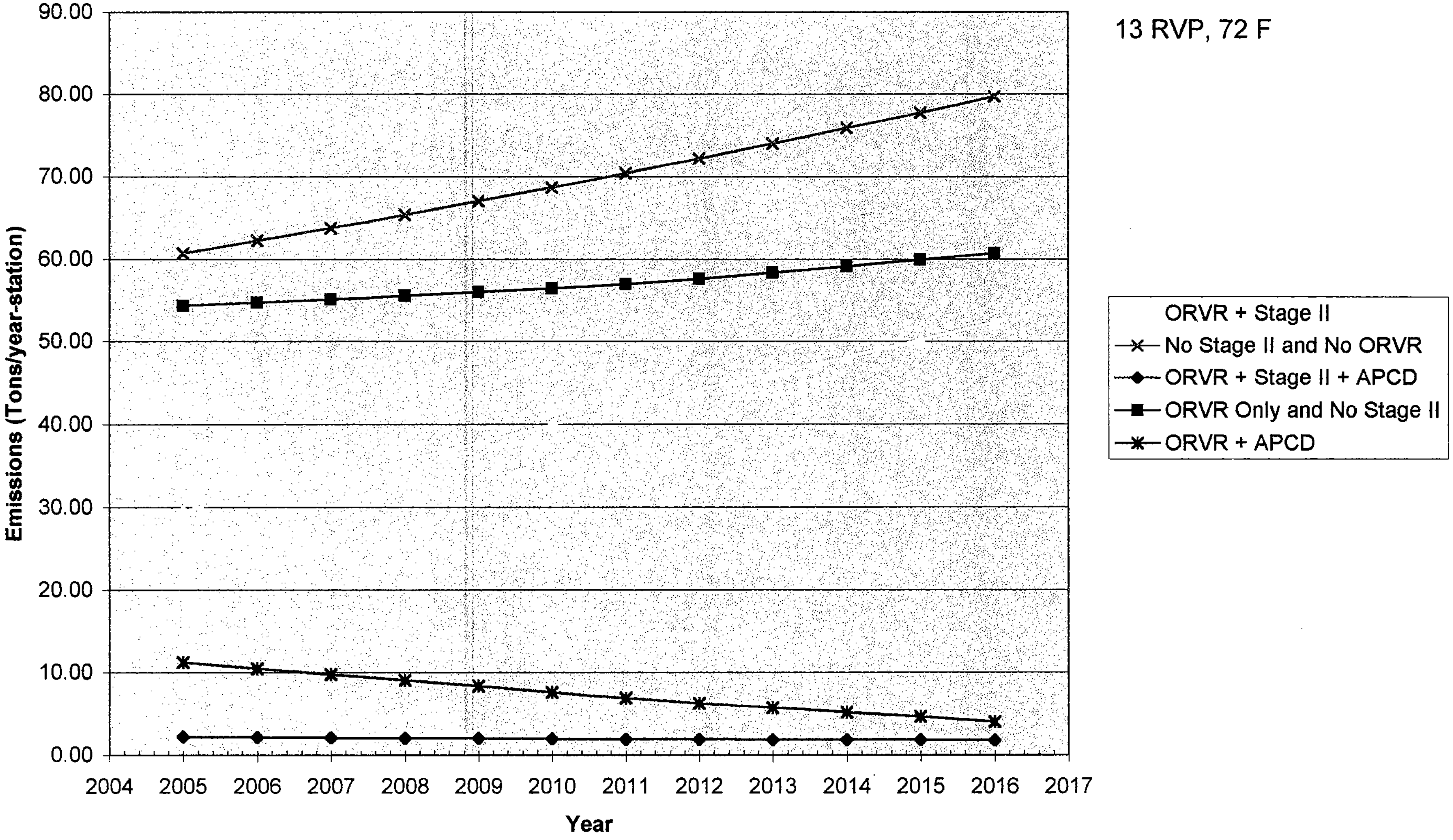


Figure 3: In-use Control Efficiency (IUE)

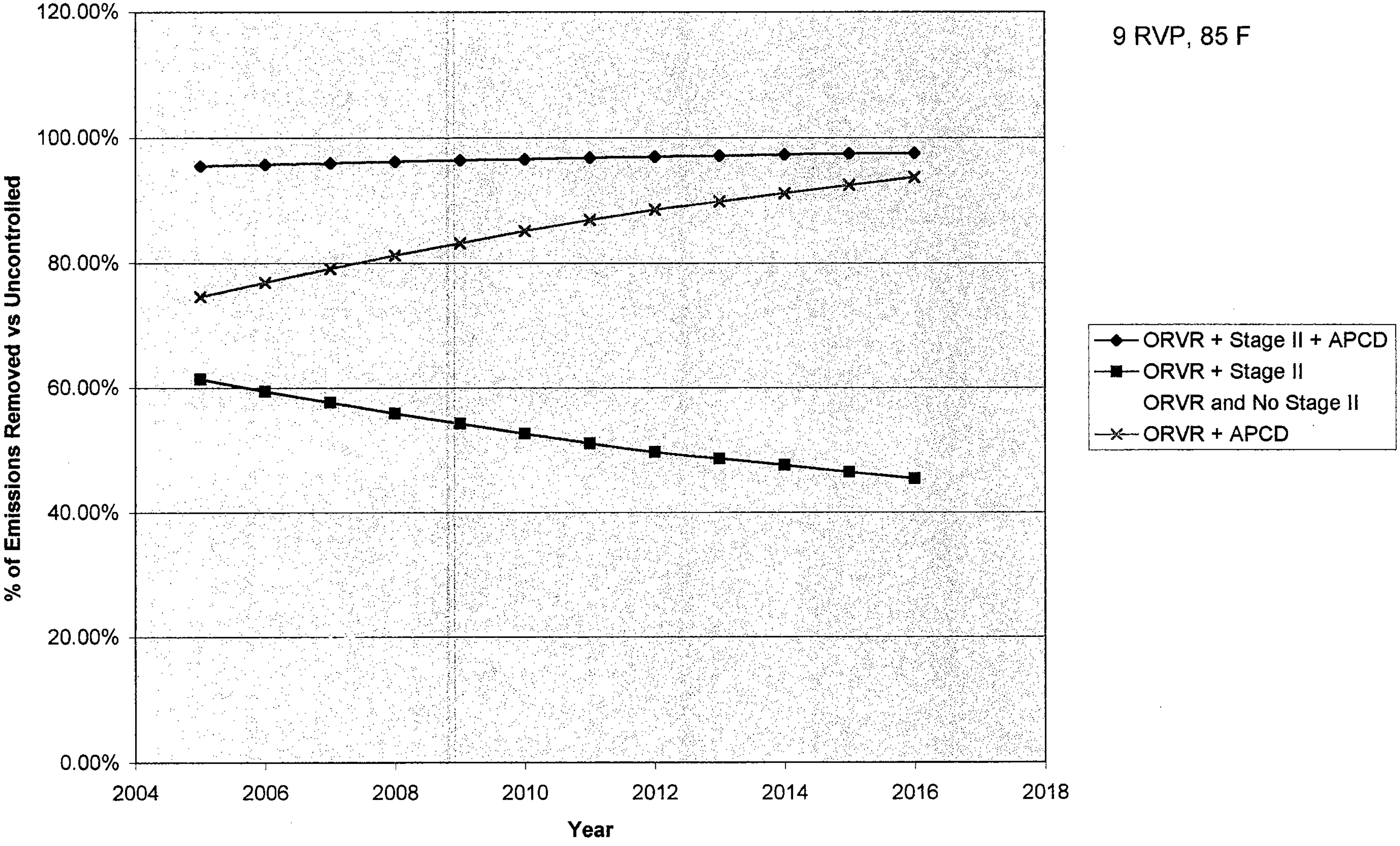
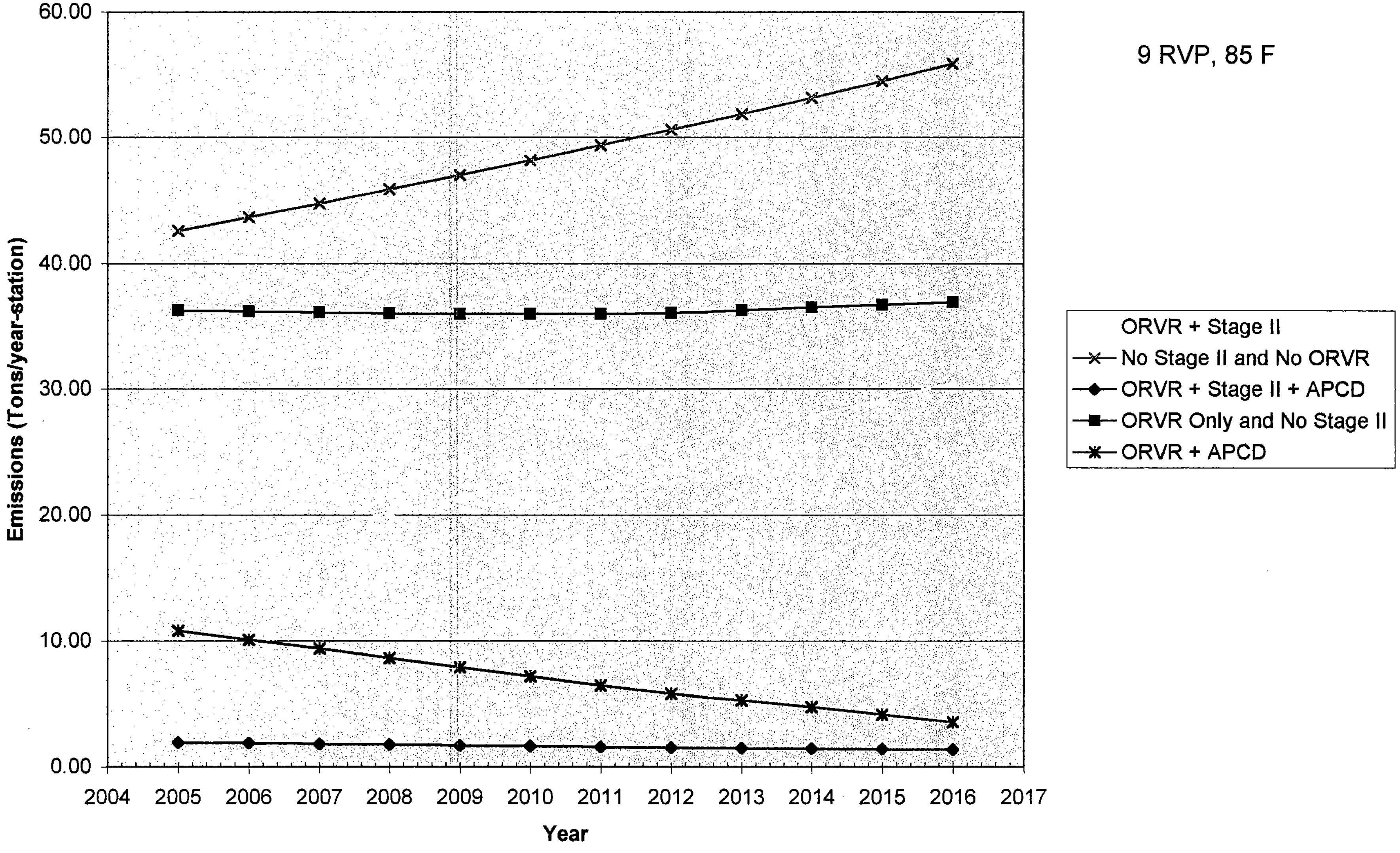


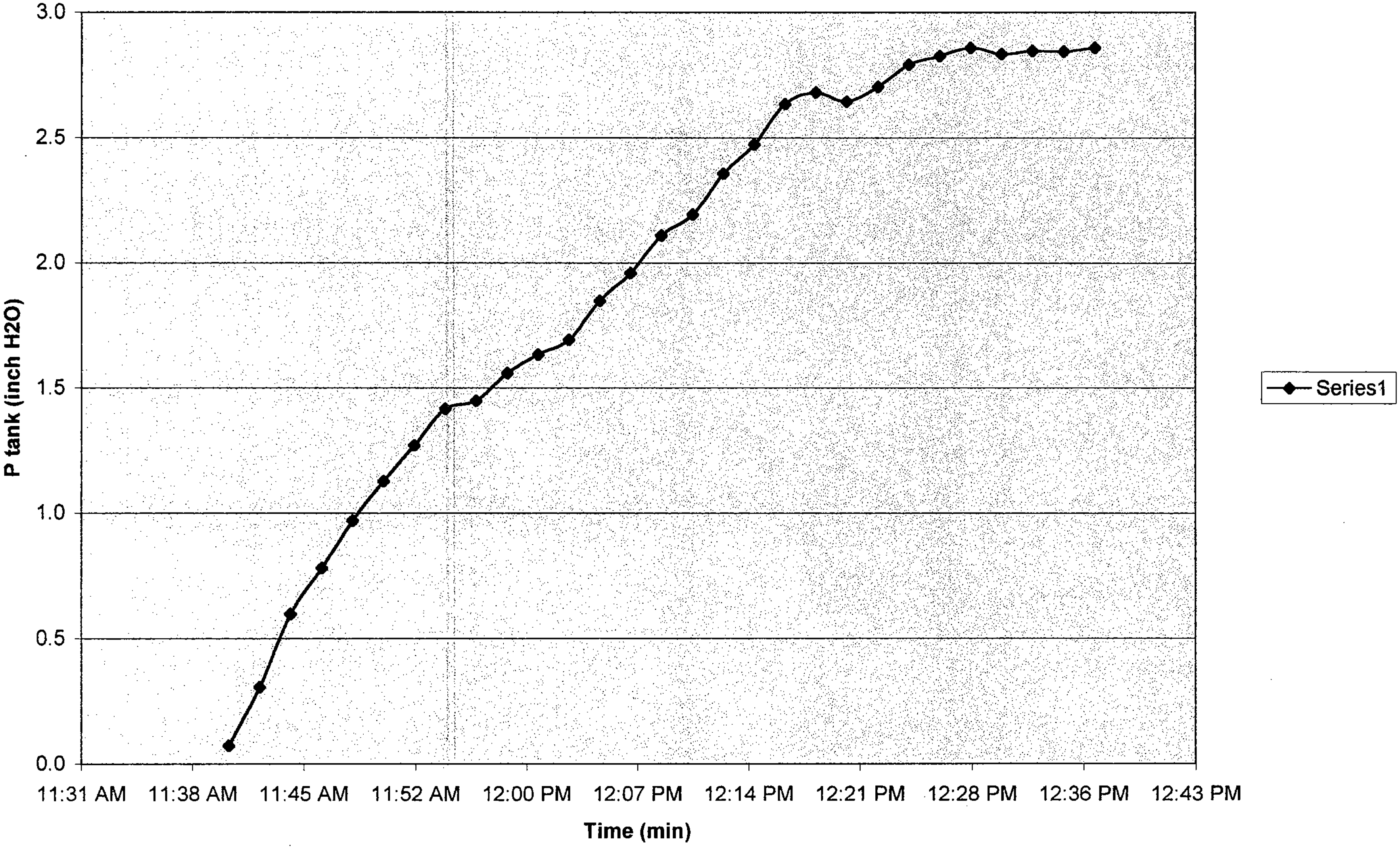
Figure 4: Storage Tank Evaporative and Vehicle Refueling Emissions at a Gasoline Dispensing Facility



Appendix 2
Measured Incompatibility Excess Emissions (IEE) – Method 1

Pressure vs Time: 2 May 2004

Lantana, Florida



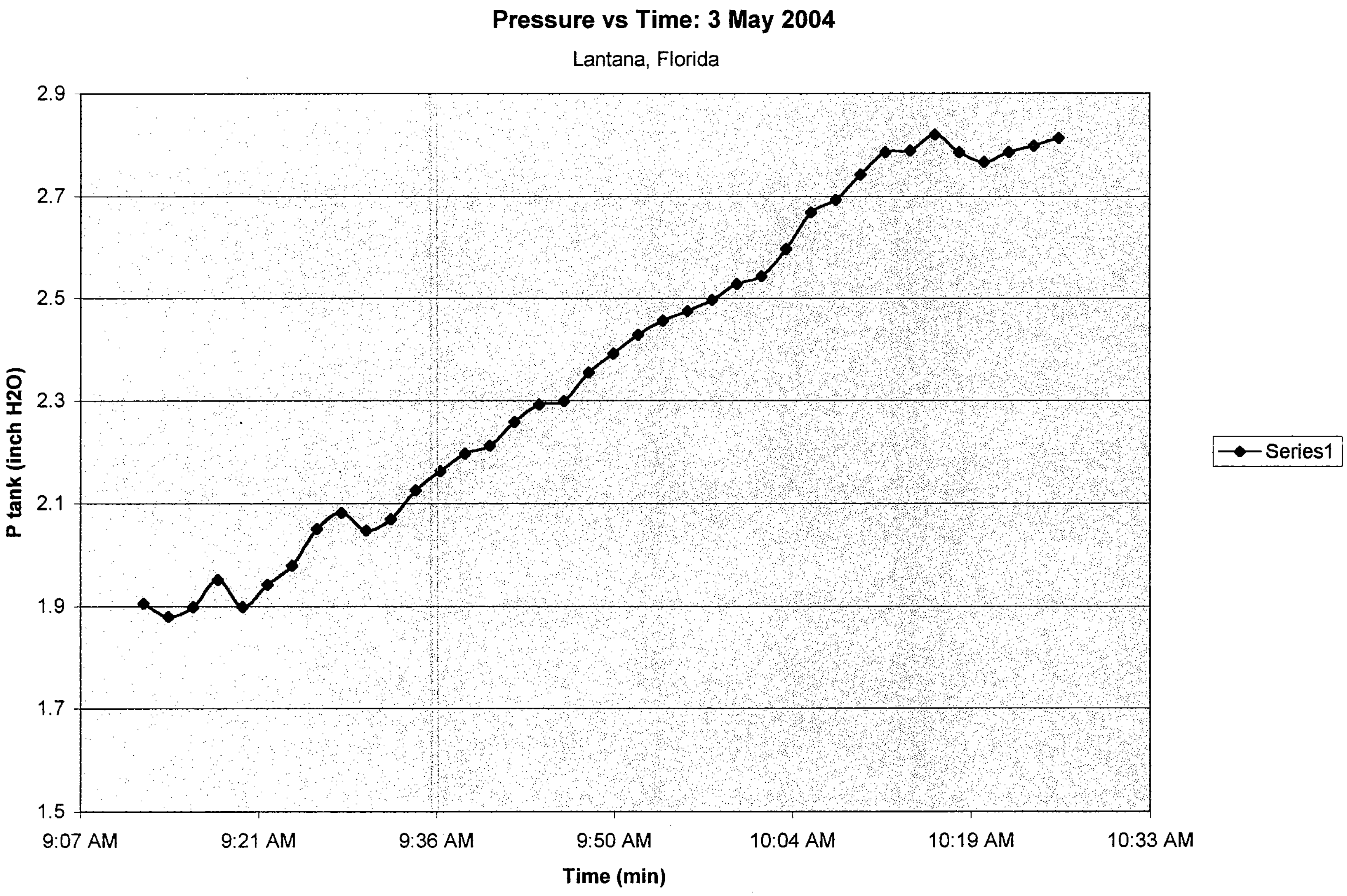
Baseline Evaporative Loss Data: Preliminary Data Set based on approximately 1 hour of data collection on 2 May 2004
SN80726

Date	P atm in H2O	P tank in H2O	**T1:Unleaded** gallons of gasoline	**T2:Unleaded** gallons of gasoline	**T3:Premium** gallons of gasoline	Total	Ullage (gal)	Ullage (ft3)	Vapor Volume Contained within Ullage (ft3)
5/2/2004 11:28	408.2752	0.741292							
5/2/2004 11:30	408.2752	0.493061							
5/2/2004 11:32	408.2752	0.790939							
5/2/2004 11:34	408.2752	0.725778							
5/2/2004 11:36	408.2752	8.97E-02							
5/2/2004 11:38	408.2153	6.18E-02	T1, T2, and T3 data taken from Veeder-Root Tank Gauge						
5/2/2004 11:40	408.2153	7.42E-02							
5/2/2004 11:42	408.2752	0.306887	14399	15748	15213	**45360**	**14640**	1957.2	1958.7
5/2/2004 11:44	408.2752	0.598559							
5/2/2004 11:46	408.2752	0.78163	14392	15707	15188	**45287**	**14713**		
5/2/2004 11:48	408.2752	0.970907							
5/2/2004 11:50	408.2752	1.126051							
5/2/2004 11:52	408.2752	1.268785							
5/2/2004 11:54	408.2752	1.414621							
5/2/2004 11:56	408.2752	1.448753	14351	15483	15078	**44912**	**15088**		
5/2/2004 11:58	408.2752	1.557354							
5/2/2004 12:00	408.2752	1.631823							
5/2/2004 12:02	408.2153	1.690778							
5/2/2004 12:04	408.2153	1.845923							
5/2/2004 12:06	408.2153	1.957628	14308	15294	14978	**44580**	**15420**		
5/2/2004 12:08	408.1554	2.109669							
5/2/2004 12:10	408.1554	2.193448							
5/2/2004 12:12	408.1554	2.354798							
5/2/2004 12:14	408.1554	2.472708							
5/2/2004 12:16	408.0955	2.634059	14195	15109	14873	**44177**	**15823**		
5/2/2004 12:18	408.0955	2.680602							
5/2/2004 12:20	408.0955	2.643368							
5/2/2004 12:22	408.0955	2.702323							
5/2/2004 12:24	408.0955	2.792307							
5/2/2004 12:26	408.0955	2.826438	14083	14923	14777	**43783**	**16217**	2168.0	2183.1
5/2/2004 12:28	408.0955	2.86057							
5/2/2004 12:30	408.0955	2.835747							
5/2/2004 12:32	408.0955	2.848159							
5/2/2004 12:34	408.0955	2.845056							
5/2/2004 12:36	408.0955	2.86057	**14093**	14753	14704	**43550**	**16450**	2199.2	2214.6

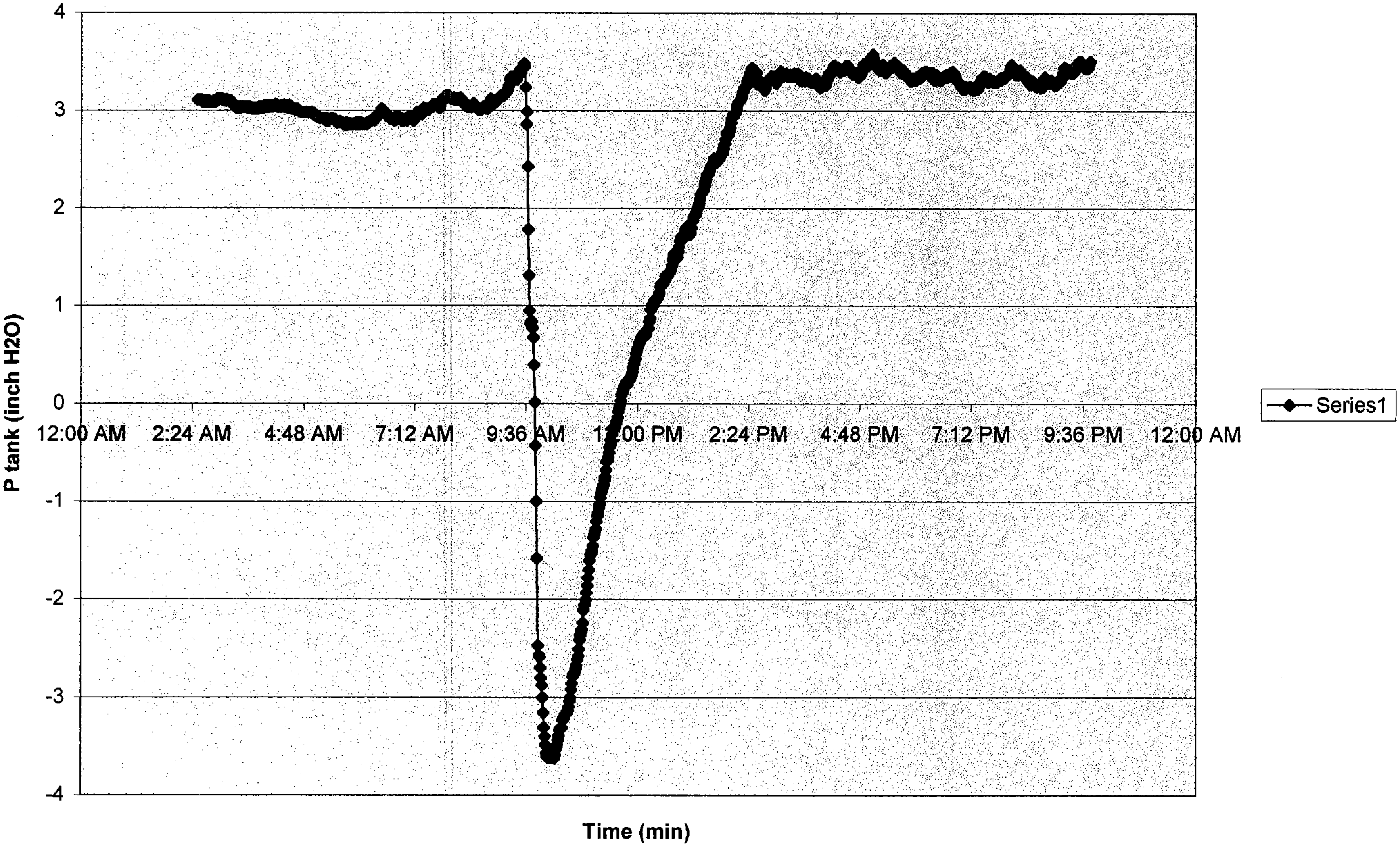
Gallons of gasoline dispensed in interval above	Average gallons/hr of gasoline dispensed in interval	Time Interval, min	Vapor volume increase in interval, ft3	CFM, ft3 per minute of vapor volume increase	lbm/min	lbm/hr	gal/hr	gal/day	gal/mo of gasoline lost to evaporation	% of Throughput Lost
1810	2011.11	54	255.92	4.74	0.24	14.59	2.81	67.32	**2019.64**	0.40%
1577	2150.45	44	224.37	5.10	0.26	15.69	3.02	72.44	**2173.09**	0.43%

Comments/Assumptions:

Molecular Weight of gasoline vapor = 66
Concentration of vapors escaping system = 30% by volume


Pressure vs Time: 3 May 2004
Lantana, Florida
P tank (inch H2O)
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
9:07 AM
9:21 AM
9:36 AM
9:50 AM
10:04 AM
10:19 AM
10:33 AM
Time (min)
Series1

Interval	Gallons	Gal/hr	Ft3	Time	Ft3/min	lbm/min	lbm/hr	gal/hr	gal/day	gal/mo	% Throughput
A-C	2015	1633.784	278.802	74	3.767595	0.19326	11.5956	2.229924	53.51817	1605.545	**0.321%**
A-B	1367	1577.308	189.662	52	3.647346	0.187092	11.22551	2.158752	51.81005	1554.302	**0.311%**



Pressure vs Time: 20 March 2004

Grass Valley, California

Evaporative Emission Rate
Grass Valley, CA Site

Ullage	gal Assumed ullage @ t0	P initial	P final	gal Vol @ P i	gal Vol @ P f	P atm	gal Delta V
30000	18000	-3.5246	3.0206	17830.7741	21222.9618	374.9	3392.18769
30000	15000	-3.5246	3.0206	14858.9784	18198.7905	374.9	3339.81212

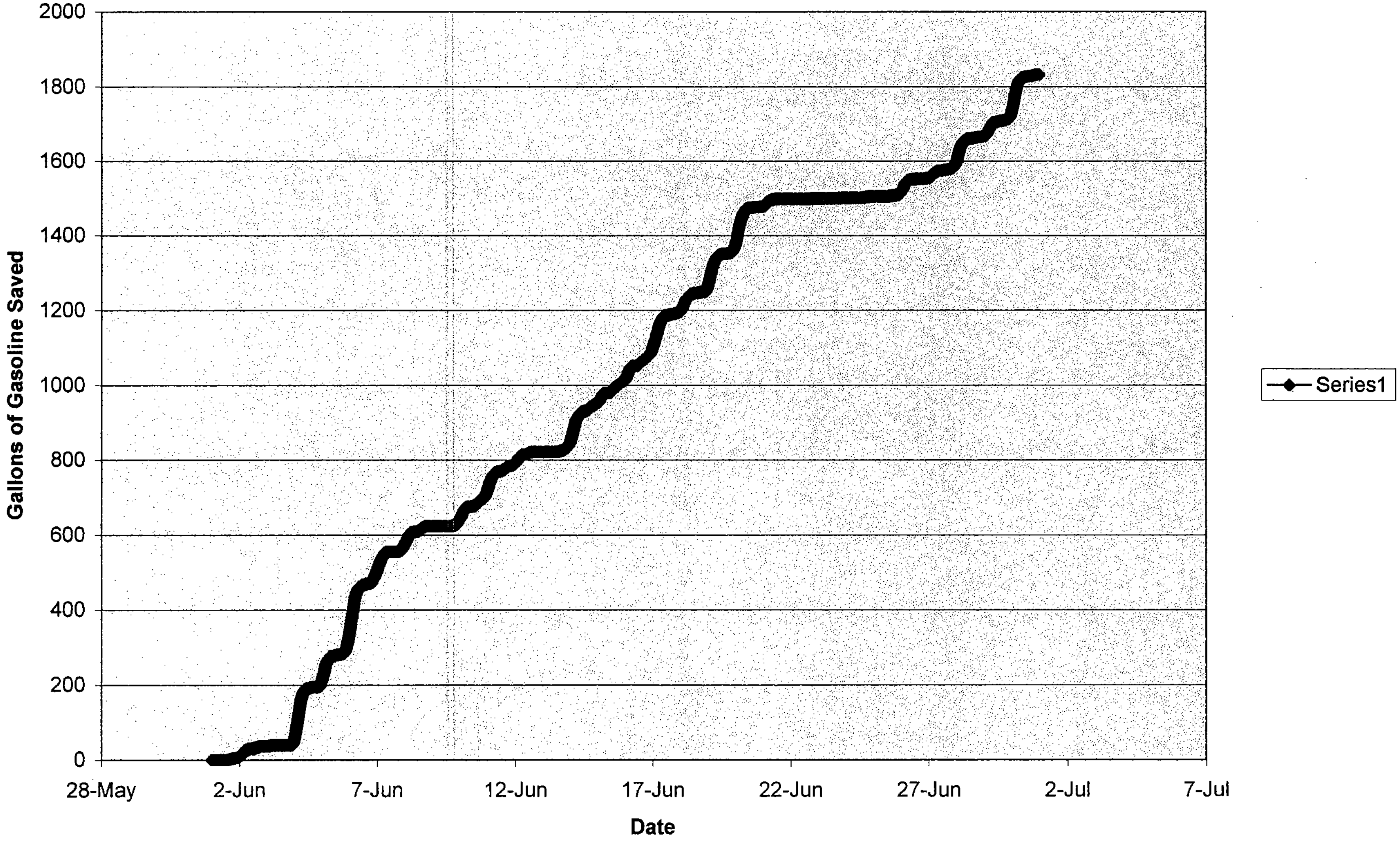
Average monthly throughput: 330,000 gallons

ft3	**min**							
	Time	**CFM**	**lb HC/min**	**lb HC/hr**	**lb HC/day**	**gal/day**	**gal/mo**	**Tons/year**
453.5010282	229	1.98035383	0.12867169	7.72030169	185.28724	35.6321616	1068.96485	33.3517033
446.4989471	229	1.94977706	0.126685	7.6010998	182.426395	35.0819991	1052.45997	32.8367511

Appendix 3
Measured Incompatibility Excess Emissions (IEE) – Method 2

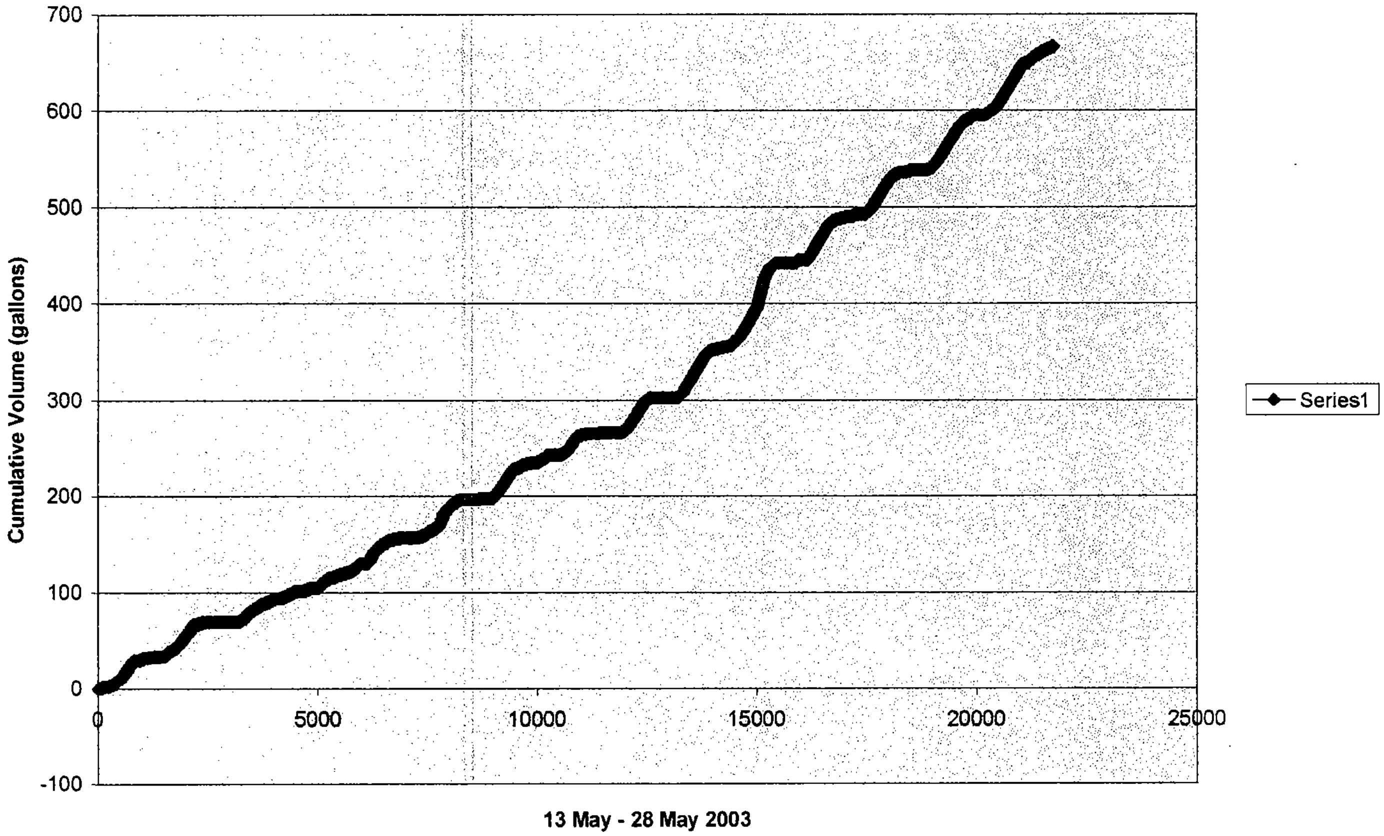
Cumulative Gasoline Saved: 1 June - 30 June 2004

Lantana, Florida



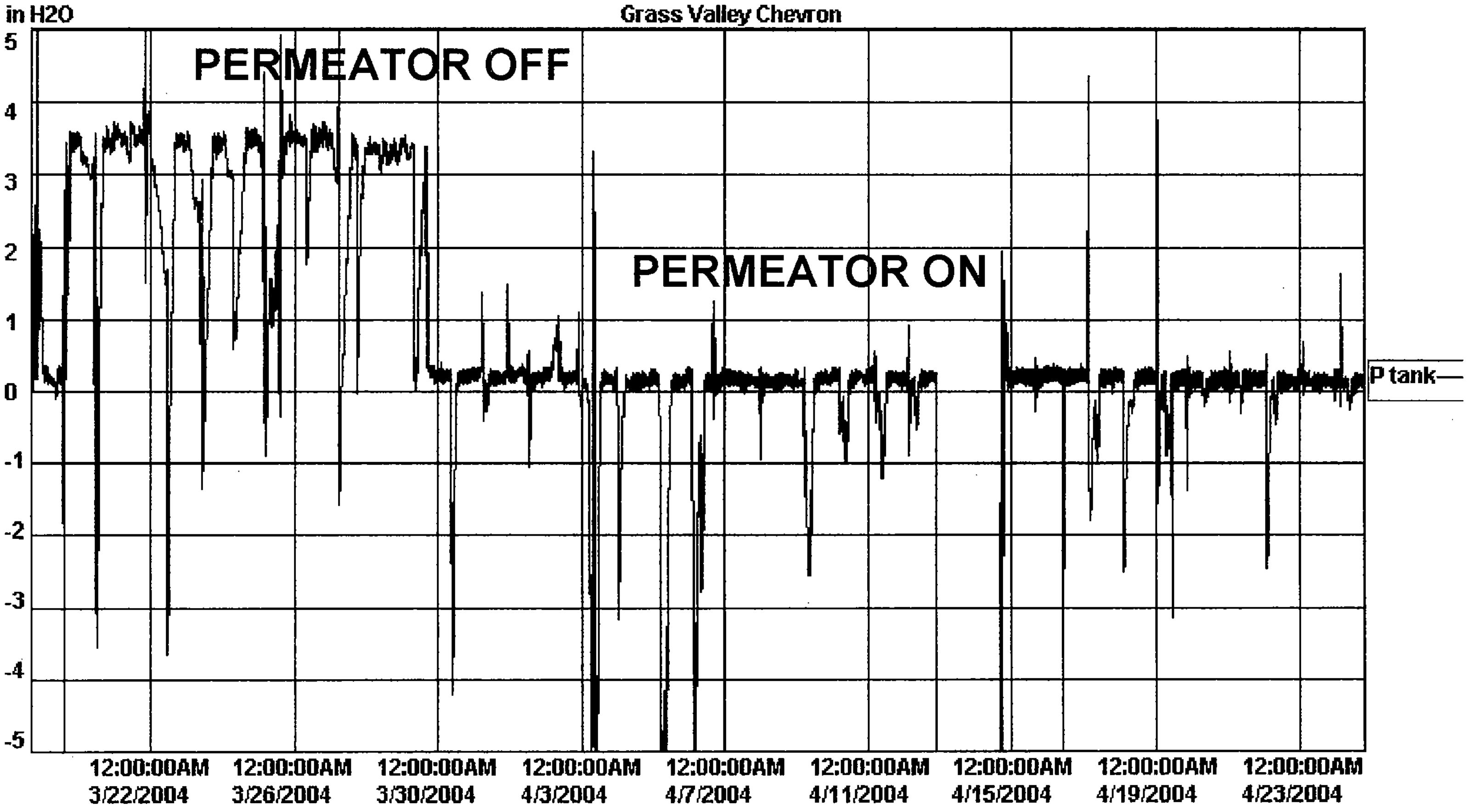
Gasoline Savings

Grass Valley, CA



Monthly Savings	**1332.89**	**gallons**
% Throughput	**0.404%**	
lbm/1,000 gallons	**21.003**	

Appendix 4
Grass Valley Chevron
Storage Tank Pressure Plot
PERMEATOR "OFF" vs. PERMEATOR "ON"


Grass Valley Chevron
in H2O
5
4
3
2
1
0
-1
-2
-3
-4
-5
PERMEATOR OFF
PERMEATOR ON
P tank
12:00:00AM 3/22/2004
12:00:00AM 3/26/2004
12:00:00AM 3/30/2004
12:00:00AM 4/3/2004
12:00:00AM 4/7/2004
12:00:00AM 4/11/2004
12:00:00AM 4/15/2004
12:00:00AM 4/19/2004
12:00:00AM 4/23/2004

Appendix 5
Increased Emissions in the Vicinity of Gasoline Dispensing Facilities
Health Impact of HAPS From Emissions

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Keyword(s)
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Occupational and Environmental Medicine 2004;**61**:773-778

ORIGINAL ARTICLE

Acute childhood leukaemia and environmental exposure to potential sources of benzene and other hydrocarbons; a case-control study

C Steffen[1], M F Auclerc[2], A Auvrignon[3], A Baruchel[2], K Kebaili[4], A Lambilliotte[5], G Leverger[3], D Sommelet[6], E Vilmer[7], D Hémon[1] and J Clavel[1]

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[2] Department of Pediatric Hematology, Saint-Louis Hospital, Paris, France
[3] Department of Pediatric Hematology, Armand Trousseau Hospital, Paris, France
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[6] Department of Pediatric Hematology, Brabois Hospital, Nancy, France
[7] Department of Pediatric Hematology-Immunology, Robert Debré Hospital, Paris, France

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Dr J Clavel
Inserm U170, 16 avenue Paul Vaillant-Couturier, 94807 Villejuif cedex, France; clavel@vjf.inserm.fr

Aim: To analyse the association between potential environmental exposure to hydrocarbons and the risk of acute childhood leukaemia.

Methods: A hospital based multicentre case control study, stratified on centre, age, and sex, with 280 leukaemia cases and 285 controls was carried out. Data were collected by a standardised interview of the mothers.

Results: No clear association was seen between maternal occupational exposure to hydrocarbons during pregnancy and leukaemia, or between residential traffic density and leukaemia. There was an association between dwellings neighbouring a petrol station or a repair garage during childhood and the risk of

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childhood leukaemia (OR 4.0, 95% CI 1.5 to 10.3), with a duration trend. The association, which appeared particularly strong for acute non-lymphocytic leukaemia (OR 7.7, 95% CI 1.7 to 34.3), was not altered by adjustment for potential confounding factors.

Conclusions: Results showed an association between acute childhood leukaemia and dwellings neighbouring auto repair garages and petrol stations, which are benzene emitting sources. These findings could be due to chance, although the strength of the association and the duration trend are arguments for a causal association.

Abbreviations: AL, acute leukaemia; ALL, acute lymphocytic leukaemia; ANLL, acute non-lymphocytic leukaemia

Keywords: leukaemia; childhood; environment; epidemiology; hydrocarbons

Related articles in Occup Environ Med:

Work in brief
Dana Loomis
Occup Environ Med 2004 61: 727. [Extract] [Full Text]

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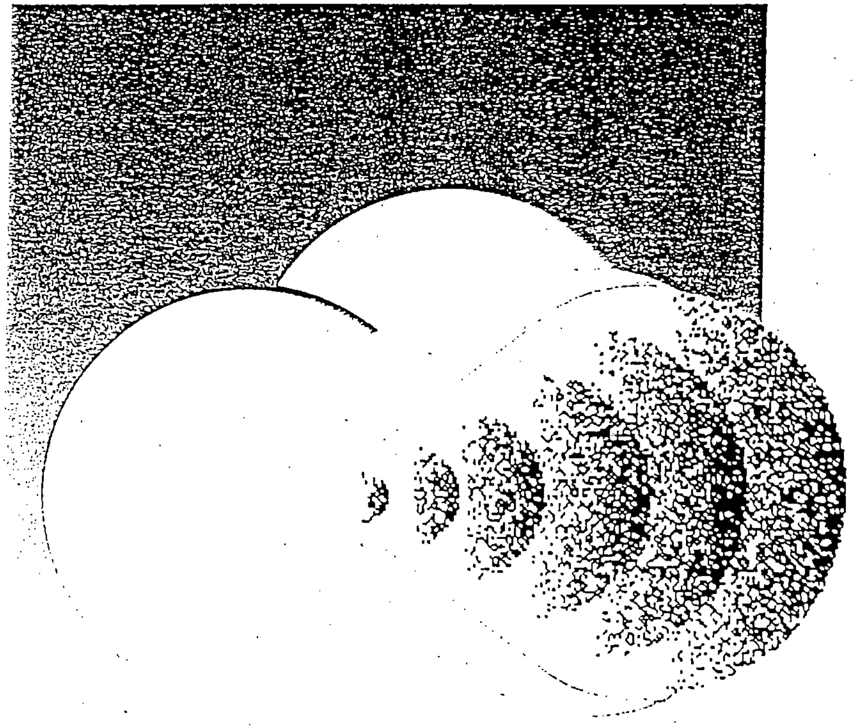
ENVIRONMENT INSTITUTE

BENZENE, TOLUENE AND XYLENE MEASUREMENTS IN THE VICINITY OF PETROL STATIONS



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BENZENE, TOLUENE AND XYLENE MEASUREMENTS IN THE VICINITY OF PETROL STATIONS

P. Pérez Ballesta, E. De Saeger
European Commission
Joint Research Centre
Environment Institute - ERLAP
I-21020 Ispra (VA) - Italy

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Introduction

It is estimated that 35 % of the anthropogenic volatile organic compound (VOC) emissions are due to vehicle exhaust and evaporative losses [1]. In urban areas the contribution to the VOC emissions from traffic may reach 60 - 80 % of the total emissions. VOCs play an important role in the formation of photochemical smog, and benzene in particular is known to be a cancerogenic agent. Therefore, there is no doubt that good air quality in cities depends on the control of VOC emissions. Regardless of the policies adopted by individual countries in the European Union, several EC directives have been implemented in order to control the emissions, e.g., catalytic converters have been installed to limit car emissions [2] and specifications have been formulated concerning benzene levels in petrol [3]. Recently, a new directive has been proposed setting out guidelines for the control of VOC emissions from petrol stations. This directive also concerns the installation of vapour recovery systems at the pumps, in order to prevent the dispersion of fuel vapours into the air when refilling [4].

VOC emissions from petrol storage and distribution systems represent some 500.000 tonnes per year, i.e. 5 % of total man-made VOC emissions in the European Union. Petrol stations situated in urban areas are considered critical locations from the point of view of air quality. Evaporative losses are the principle cause of contamination around petrol stations. These losses are mainly produced during tank refilling, by the vent pipes of the storage reservoirs, as well as during accidental fuel spillages while refilling.

The objective of the campaign was to determine the impact of ambient VOC concentration levels and the grade of dispersion of VOCs emitted by petrol stations in urban agglomerations.

Contents

Selection of the contaminants

The diversity of contaminants emitted by petrol due to evaporation depends on its composition. About 95 % of the vapour emissions from petrol derive from paraffinic (80 %) and olefinic (15 %) compounds; the remaining 5 % from aromatic compounds [5]. The latter compounds have proven to be the most important because of their carcinogenic effect and their higher percentage levels in unleaded fuels. The carcinogenic effect between the monoaromatic hydrocarbons is demonstrated for benzene. Compounds such as toluene, xylenes, ethyl benzene, 1,2,4-methyl benzene cause an increase in the number of overall malignant tumours [6].

The composition of fuel vapour is directly related to its liquid composition. It is known that unleaded petrol contains a high proportion of aromatic hydrocarbons (between 30-45 %). Benzene, toluene and xylene (BTX) were selected as a tracer for VOCs emitted by petrol stations because of their toxic effect and their presence in fuels at a significant levels.

Sampling strategy

Approximately 20 sampling sites were selected for each petrol station. These sites were distributed in the precinct and in the surroundings of the petrol stations over an area of approximately 200 metres in diameter. In Figures 3 to 6, the positions of the samplers are indicated. The diffusive samplers were fixed to lamp-posts at a height of 3 metres above the ground and were protected from precipitation with a special cover.

Three consecutive sampling periods of fourteen days were established for each campaign - see Table II -. Diffusive samplers were collected at the end of each period.

In addition, daily analyses were carried out using active tubes in station A, B and C.The position of the active tubes is indicated in Figures 1 to 4 by a red cross.

Table II: Sampling periods during the campaign - 1994 -

Season / Period	Petrol station/city	From	To
Winter - 1st period	C and D - Brussels	January 22nd	February 5th
Winter - 2nd period	C and D - Brussels	February 5th	February 19th
Winter - 3rd period	C and D - Brussels	February 19th	March 5th
Autumm - 1st period	C and D - Brussels	September 19th	October 4th
Autumm - 2nd period	C and D - Brussels	October 4th	October 19th
Autumm - 3rd period	C and D - Brussels	October 19th	November 3rd
Autumm - 1st period	A and B - Murcia	September 25th	October 9th
Autumm - 2nd period	A and B - Murcia	October 9th	October 23rd
Autumm - 3rd period	A and B - Murcia	October 23rd	November 6th

Meteorological conditions during the campaigns

Table IV shows the meteorological conditions for the respective sampling periods and locations. A brief description of the table is given below:

Winter campaign in Brussels (January 22nd to March 5th)

The weather conditions were typical for the cold season in the North of Europe. In particular, overcast sky with rain and snow predominated during this period, with mean temperatures ranging from 0 to 10 ºC. Anticyclonic conditions with nocturnal inversions, low temperatures (as low as -8 ºC), and weak solar radiation prevailed from 13th to 20th February.

Autumm campaign in Brussels (September 19th to November 3th)

Temperatures ranged from 5 to 18 ºC with average temperature of 12 ºC. Mean wind speeds of about 3 m/s were measured. Humidities of about 80 % and a mean daily precipitation of 3.9 L/m^2 could be considered normal for this period in Brussels.

Autumm campaign in Murcia (September 25th to November 6th)

Meteorological data were available from the Murcia Meteorological Station (3 km from Murcia city). Temperatures ranged from 8 to 30 ºC with an average temperature of about 20 ºC. The average relative humidity was 80 %, the atmospheric pressure ranged between 1013 and 1018 mbar (sea level) and the mean wind speeds were between 1.6 and 1.9 m/s. Precipitations over 8 L/m^2 were only measured for four days during the first four weeks.

Table IV: Meteorological conditions for the period campaigns

Season /period	Location	Temperature, °C			RH %			Rainfall L/m^2	Aver. pressure mbar	Wind					
										Direction frequency, %					Average speed m/s
										First quarter	Second quarter	Third quarter	Fourth quarter	Calm	
		Min.	Max.	Aver.	Min.	Max.	Aver.								
Autumm/1st	Murcia	13	30	20.4	40	100	77	21.4	1013.5	37.1	14.2	26	16.3	6.4	1.9
Autumm/2nd	Murcia	12	28	20.3	40	100	77	23	1017.8	25.8	13.3	28.5	22.8	9.6	1.7
Autumm/3rd	Murcia	7.6	25	17.7	36	100	81	4.2	1016.5	19.6	11.8	34.5	25.7	8.4	1.6
Autumm/1st	Brussels	10.6	18.3	14.2	77	91	84.3	17.2	NA	30.3	17.7	38.2	17.7	-	2.5
Autumm / 2nd	Brussels	5.6	14.8	9.7	63	89	76.3	0.7	NA	30.13	52.5	14.9	2.35	-	2.6
Autumm 3rd	Brussels	8.4	14.3	10.9	70	96	84	44.8	NA	1.3	21.7	75.5	1.4	-	4.7
Winter / 1st	Brussels	3.3	7.7	5.8	66	100	82	51.9	NA	3.9	12.9	58.2	24.9	-	4.8
Winter / 2nd	Brussels	-0.4	5.2	2.3	63	97	78	6.4	NA	20.5	42.4	23.8	13.2	-	3.5
Winter / 3rd	Brussels	8.1	14.3	11	63	99	84	36.7	NA	9.3	21.47	60.7	8.53	-	3.4

NA: Non Available

Table VI: Petrol station A (Murcia). Average concentrations during the autumm period ($\mu g/m^3$)

Position	benzene	toluene	m-xylene
1	21,1	60,2	32,8
2	24,8	65,0	36,1
3	25,3	66,8	48,5
4	20,9	60,9	31,7
5	20,6	56,5	32,3
6	33,3	78,7	44,1
7	27,2	63,5	42,7
8	25,5	61,1	33,6
9	39,1	83,6	49,8
10	23,7	53,1	30,8
11	121,5	218,7	93,2
12	172,4	302,9	122,4
13	177,2	316,5	116,2
14	108,3	214,0	85,3
15	23,5	61,7	37,6
16	187,6	325,1	142,4
17	144,4	286,4	119,7
18	85,5	184,4	87,9
19	13,6	36,7	20,7
20	14,7	40,6	22,0
21	11,9	34,2	19,4

Table VII: Petrol station B (Murcia). Average concentrations during the autumm period ($\mu g/m^3$)

Position	benzene	toluene	m-xylene
1	12,7	36,3	17,6
2	17,0	48,2	27,4
3	20,6	56,2	39,7
4	17,7	53,1	28,1
5	23,8	69,2	39,3
6	21,9	58,4	34,3
7	29,9	70,8	38,3
8	18,7	58,3	35,9
9	37,9	74,3	37,7
10	70,2	134,2	61,1
11	121,2	213,4	87,5
12	90,1	152,1	61,9
13	121,3	197,0	78,5
14	96,7	197,8	86,4
15	79,3	157,2	72,8
16	33,2	85,2	42,6
17	27,9	62,8	35,7
18	12,2	29,9	15,2
19	13,7	32,0	15,7
20	12,9	32,9	17,4

Table X: Petrol station C (Brussels). Average concentrations during the winter period (µg/m³)

Position	benzene	toluene	m-xylene
1	4,4	6,3	4,7
2	4,3	12,8	7,9
3	3,9	16,2	6,4
4	2,3	6,9	3,7
5	5,6	9,0	5,4
6	2,8	7,9	3,1
7	15,7	66,3	32,3
8	10,3	51,0	24,9
9	17,5	43,0	21,5
10	19,9	52,0	17,3
11	11,9	34,8	12,6
12	4,6	16,2	7,0
13	9,9	23,6	7,5
14	6,9	16,4	4,2
15	3,3	8,9	4,3
16	4,5	13,4	8,0
17	3,9	11,7	4,7
18	8,8	16,1	4,9
19	2,7	14,0	5,0

Table XI: Petrol station D (Brussels). Average concentrations during the winter period (µg/m³)

Position	benzene	toluene	m-xylene
1	4,0	10,2	2,4
2	4,1	11,2	3,0
3	4,3	12,2	3,2
4	23,4	49,8	9,7
5	4,3	12,2	3,2
6	4,0	17,7	7,9
8	13,1	33,7	9,1
9	16,3	42,1	11,3
10	17,6	42,5	11,4
11	20,3	42,2	14,2
12	6,8	31,2	12,3
13	3,4	11,1	6,1
14	4,3	13,3	7,7
15	4,4	22,5	16,9
16	3,0	13,0	7,9
18	3,8	15,8	8,3
19	–	16,4	10,1
20	4,2	17,5	9,7
21	4,2	15,6	8,1

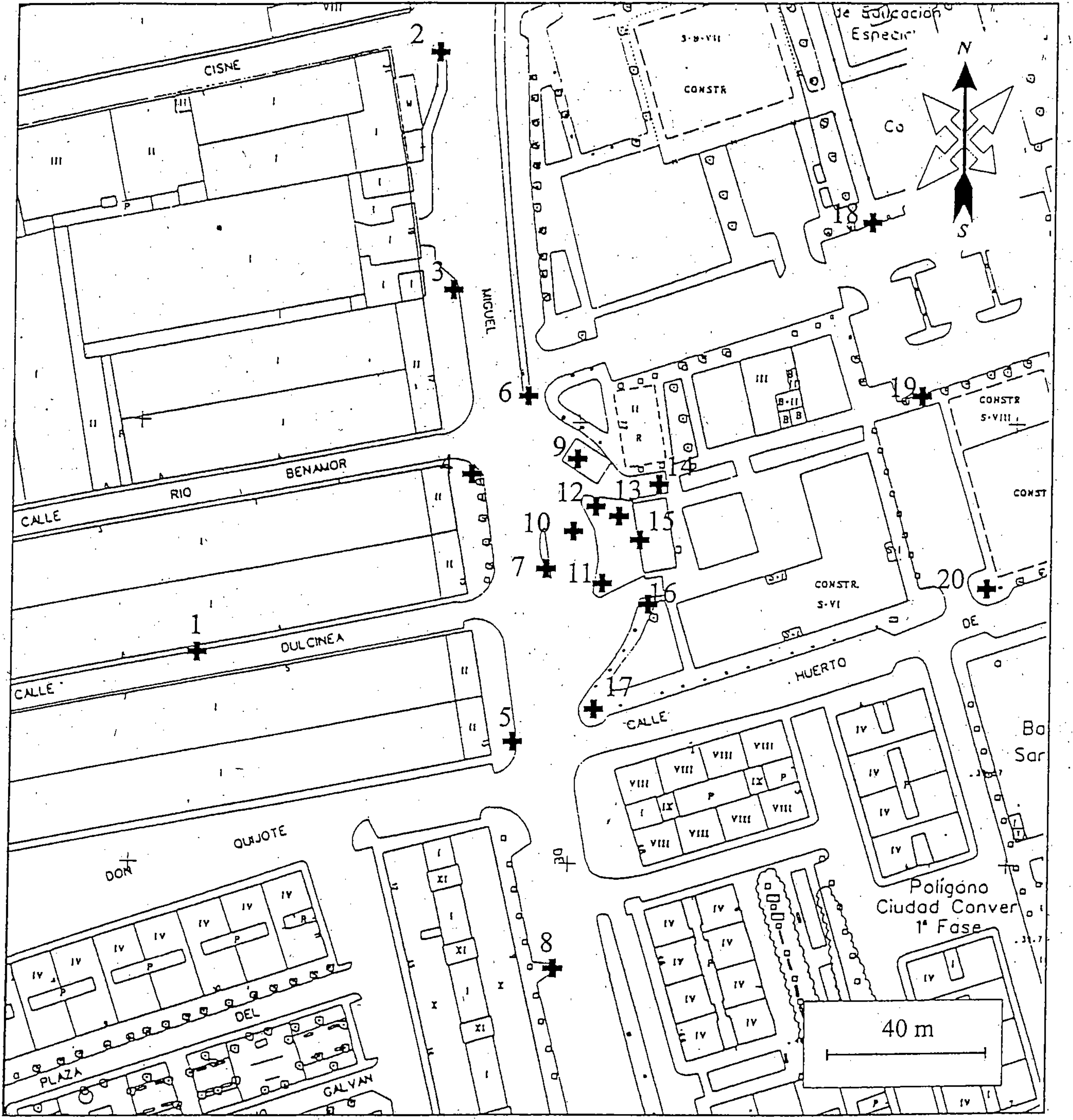

Figure 2: Diffusive samplers positions in petrol station B (Murcia)

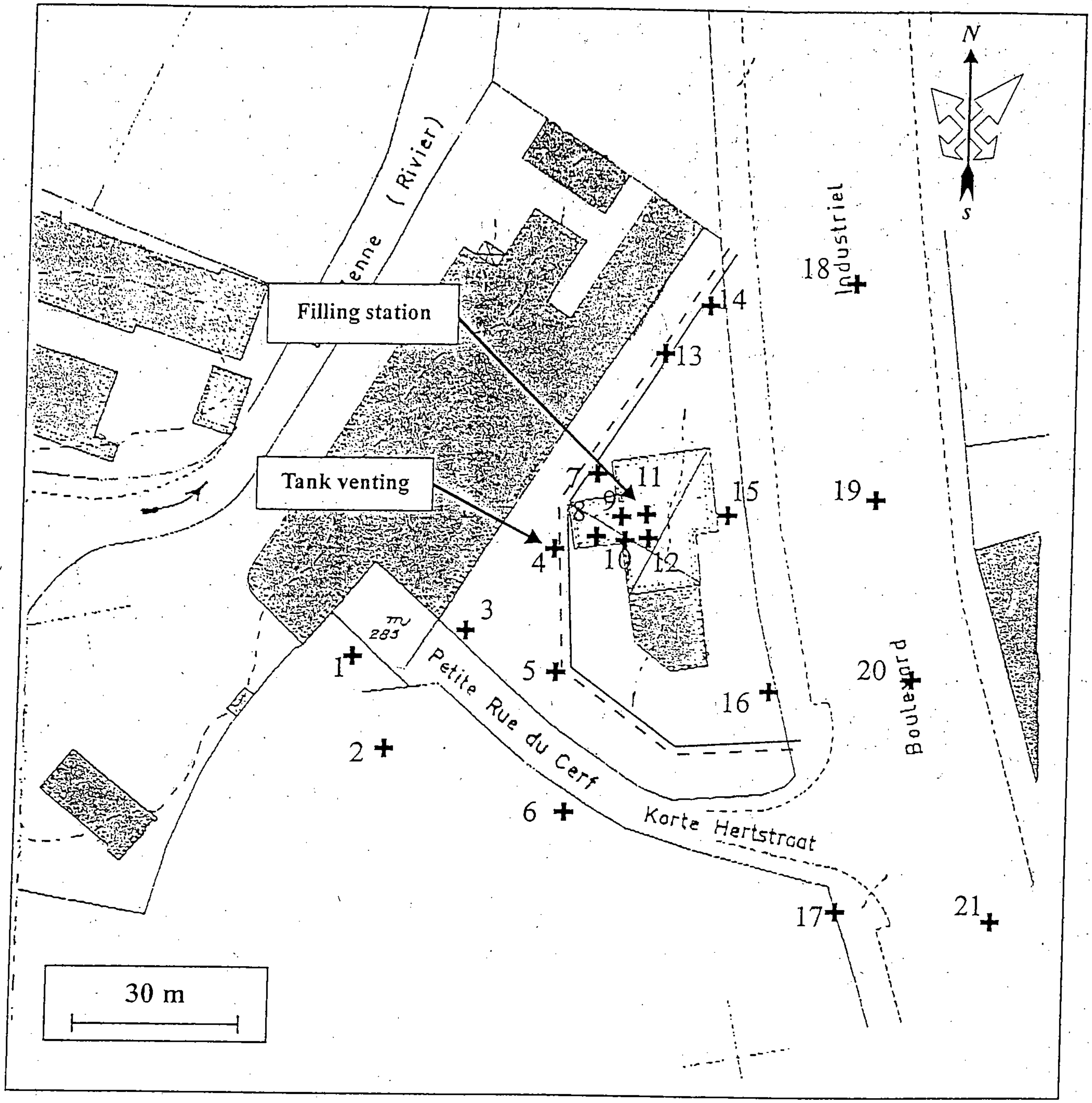

Figure 4: Diffusive samplers positions in petrol station D (Brussels)

Precision of the method

Laboratory experiments have been carried out in order to determine the sampling rates of the diffusive samplers and to establish the effect of ambient variables such as temperature, humidity, changes in concentration, influence of sampling time and concentration levels (amount of contaminants on the adsorbent). With the scope to assess the validity of the diffusion sampling technique in field conditions, duplicate active samples were also installed in a number of sites. The results of this comparison appear in the Figure 5. An acceptable correlation ($R^2 = 0.952$) was found between active and diffusive samplers that were placed in the same position.

Figure 6 represents the bias of the average concentrations estimated using the diffusive sampling technique with respect to the active sampling technique. The average bias is around -9 % and the absolute average bias is approximately 21 %. It appears that the data obtained by diffusive sampling is underestimated with respect to that obtained by active sampling. In addition, the graph shows an increase in the bias for low concentrations due to the lack of precision of the measurements near to the detection limit.

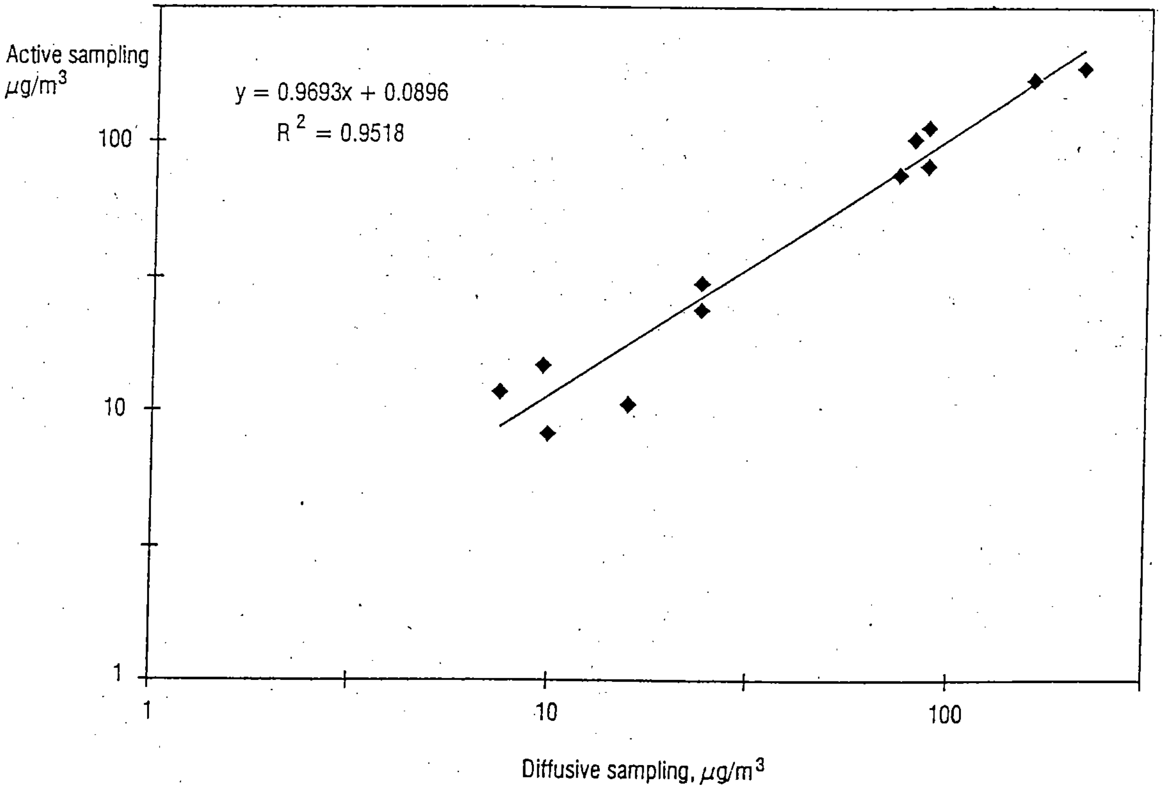

Figure 5: Correlation between active and diffusive samples

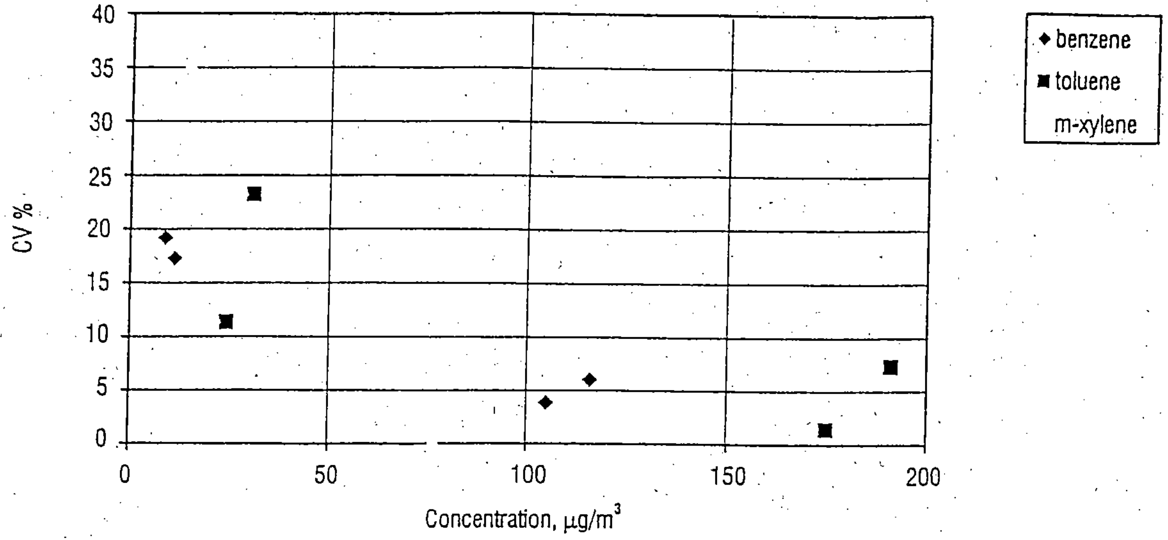

Figure 8: Active samplers' coefficients of variation between sampling periods

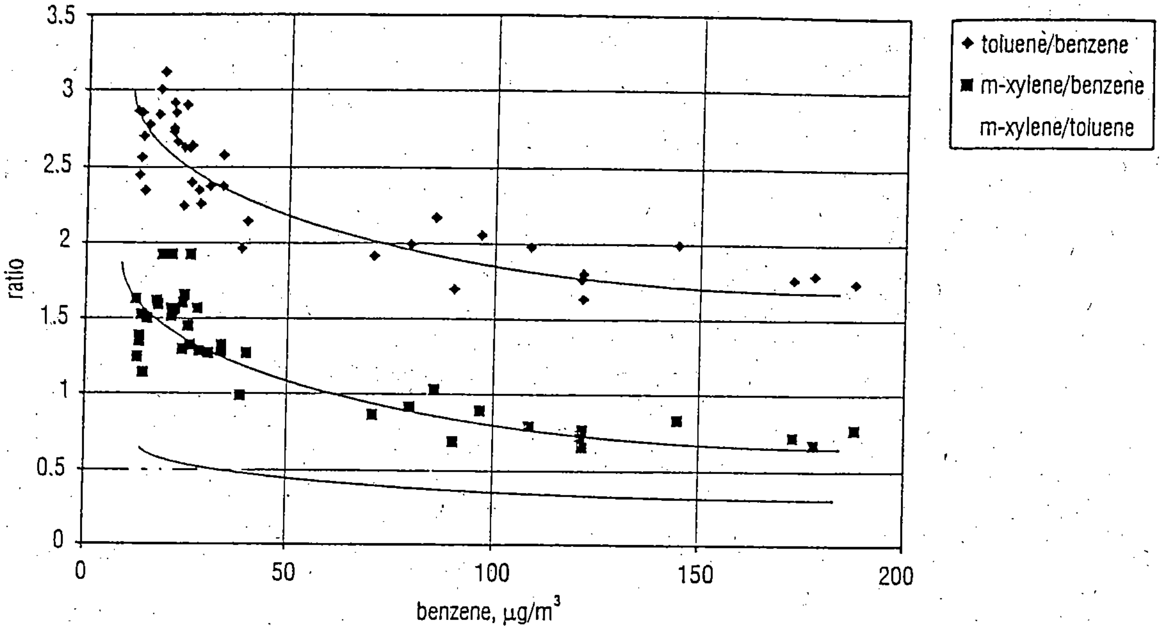

Figure 9: Toluene/benzene, m-xylene/benzene and m-xylene/toluene ratios in function of benzene concentration in Murcia

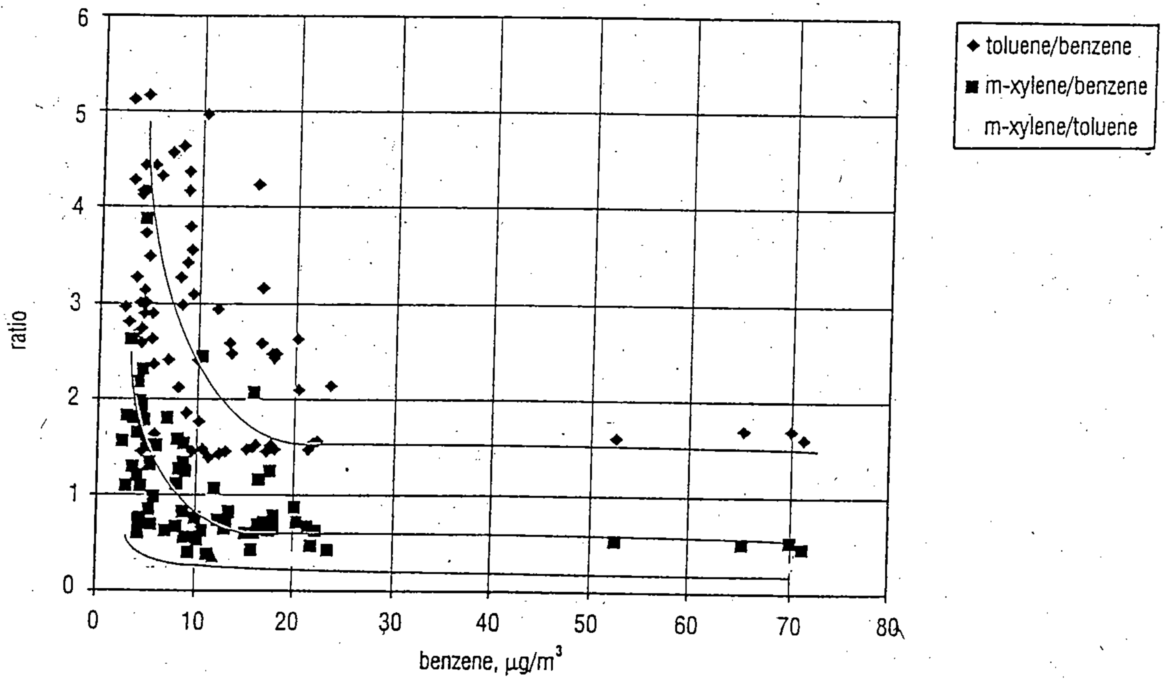

Figure 10: Toluene/benzene, m-xylene/benzene and m-xylene/toluene ratios in function of benzene concentration in Brussels

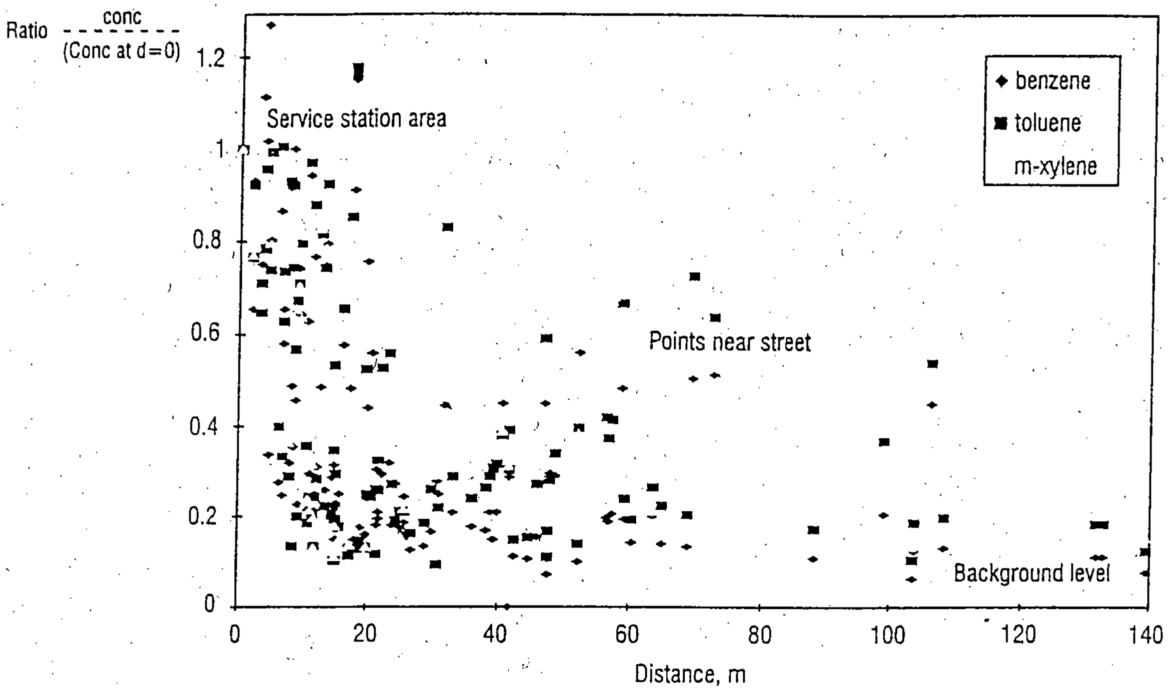

Figure 13: Variation of the airborne concentration with the distance from the service area

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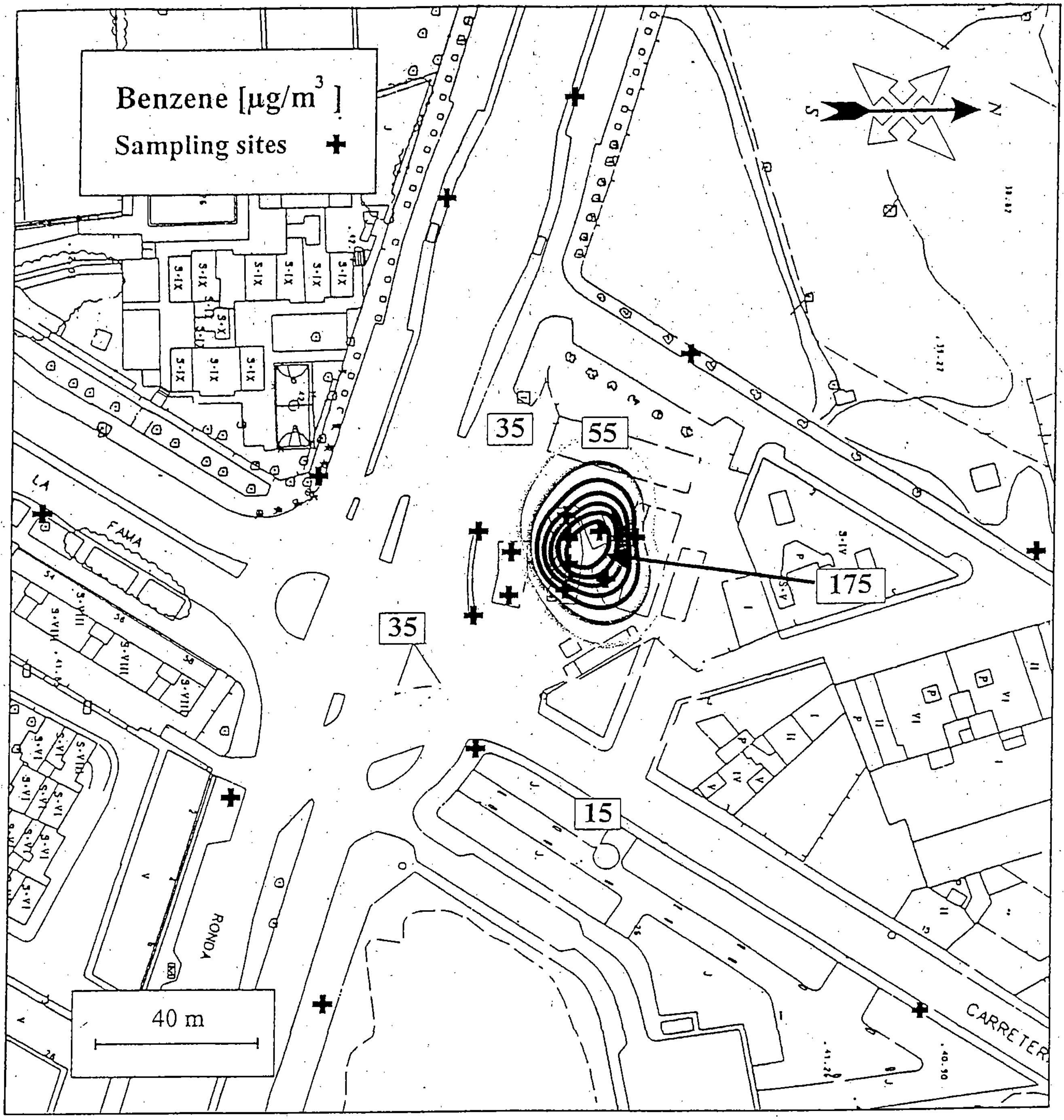
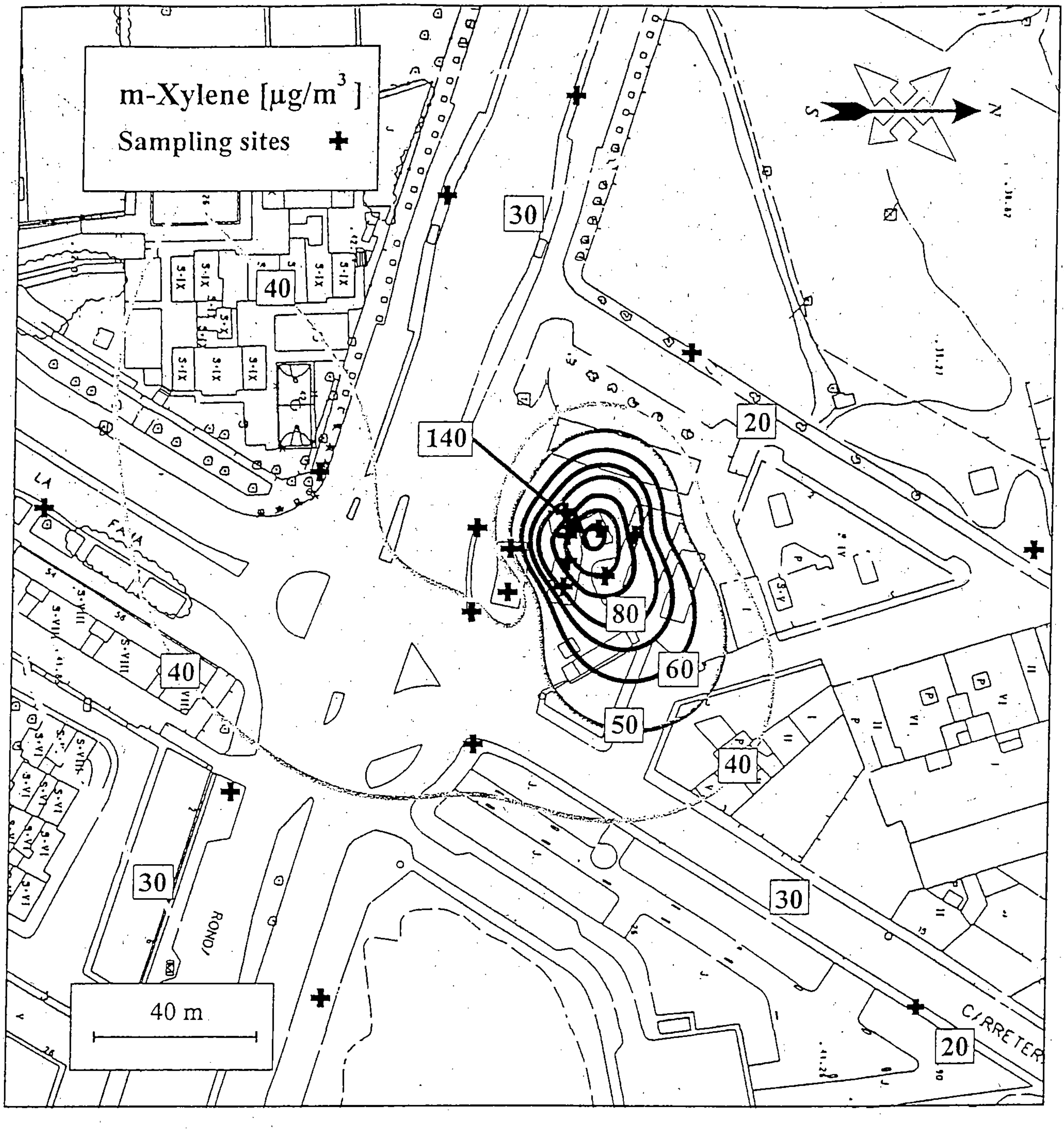
Annex 1

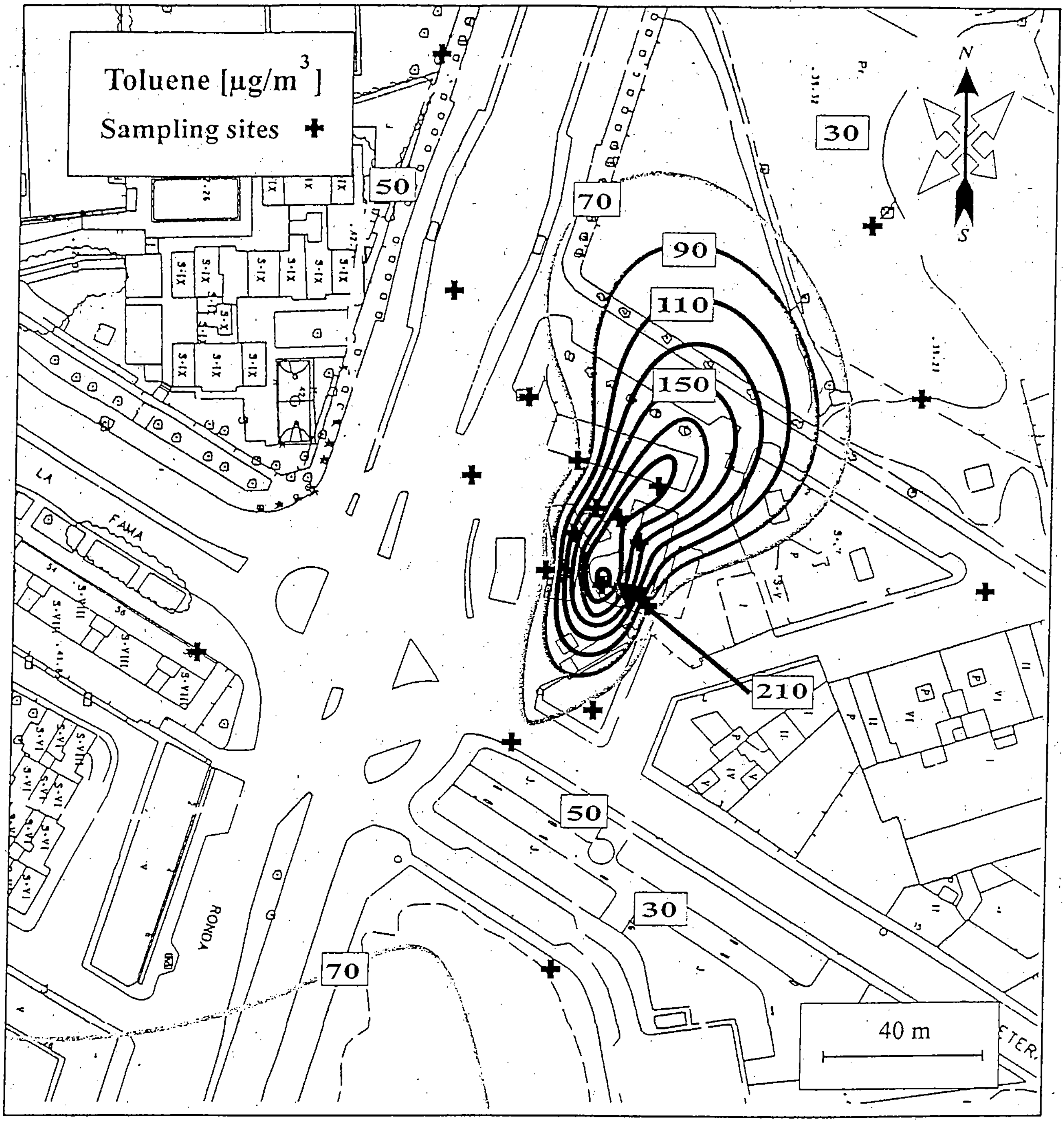
Maps of isoconcentrations



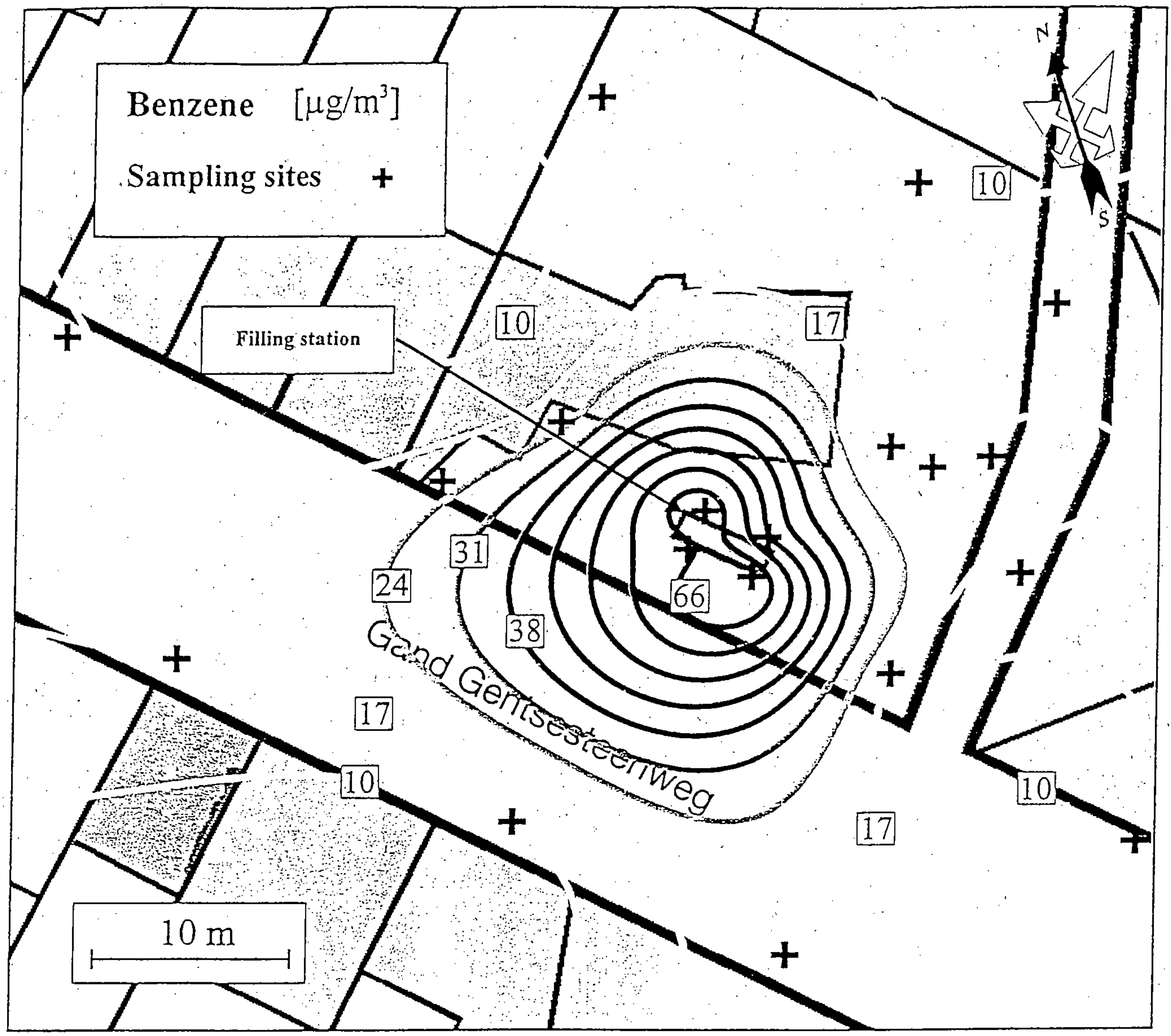
Benzene levels in petrol station A. Murcia 25/09/94 - 05/11/94



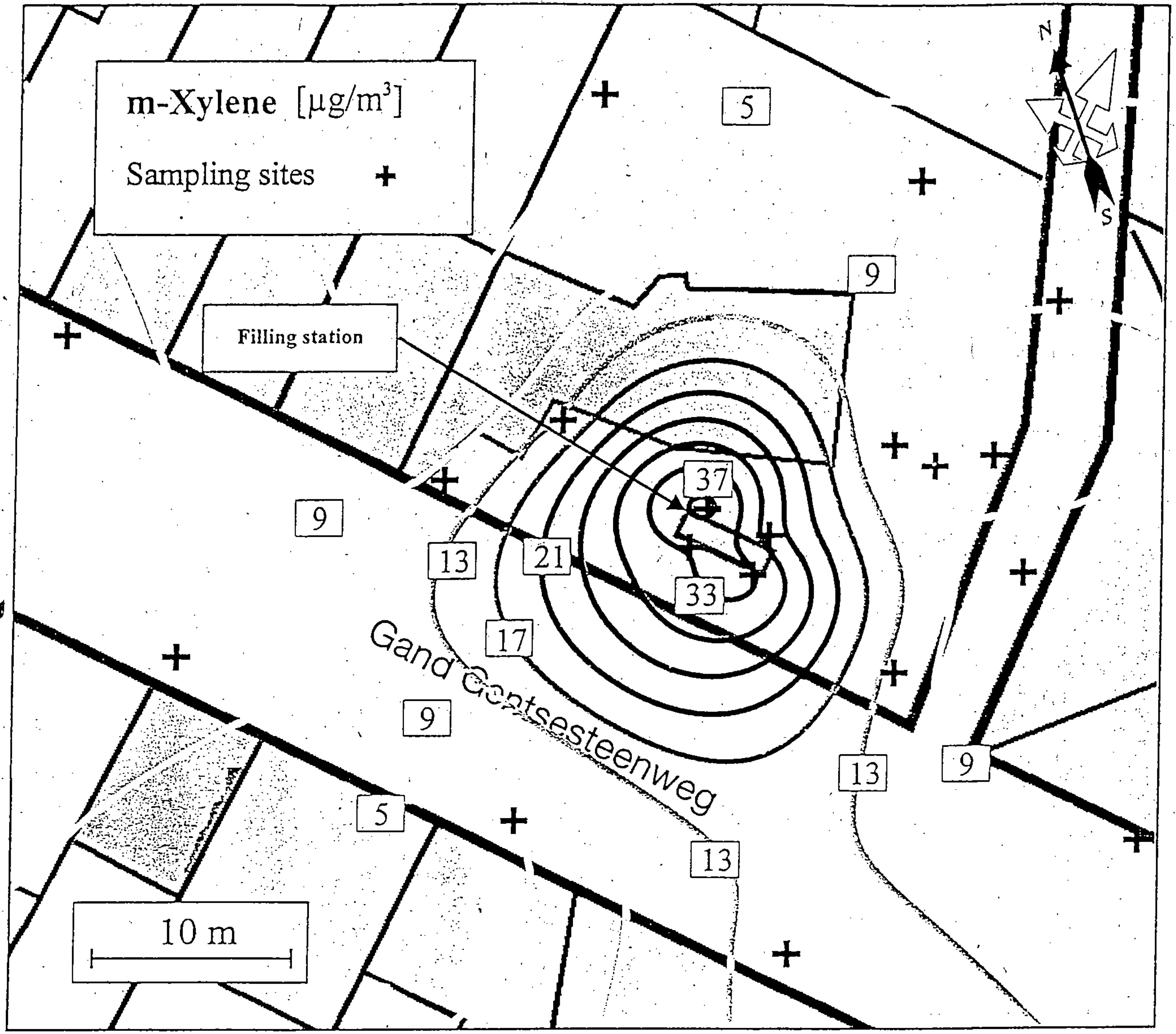
m-Xylene levels in petrol station A. Murcia 25/09/94 - 05/11/94



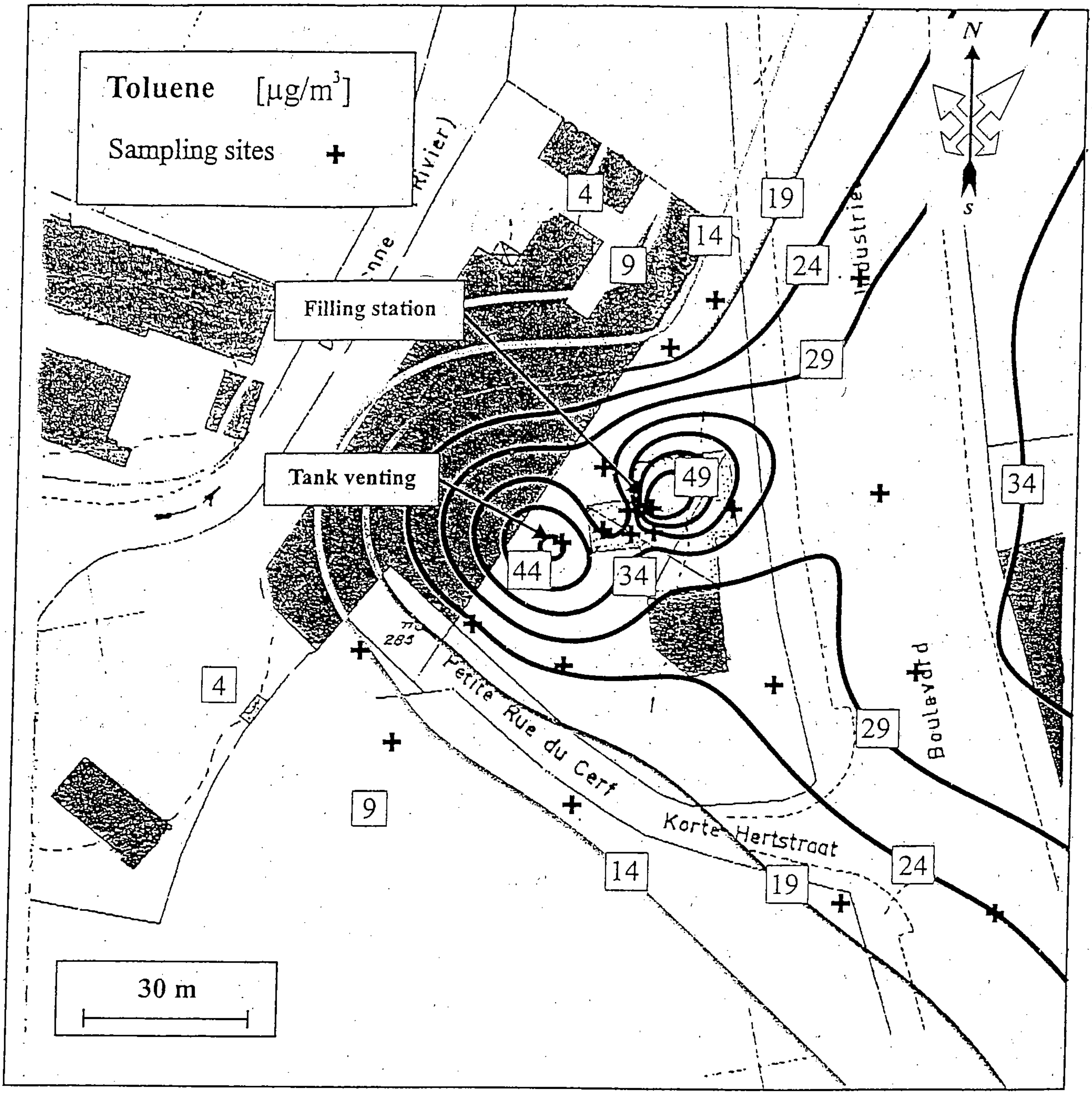
Toluene levels in petrol station B. Murcia 25/09/94 - 05/11/94



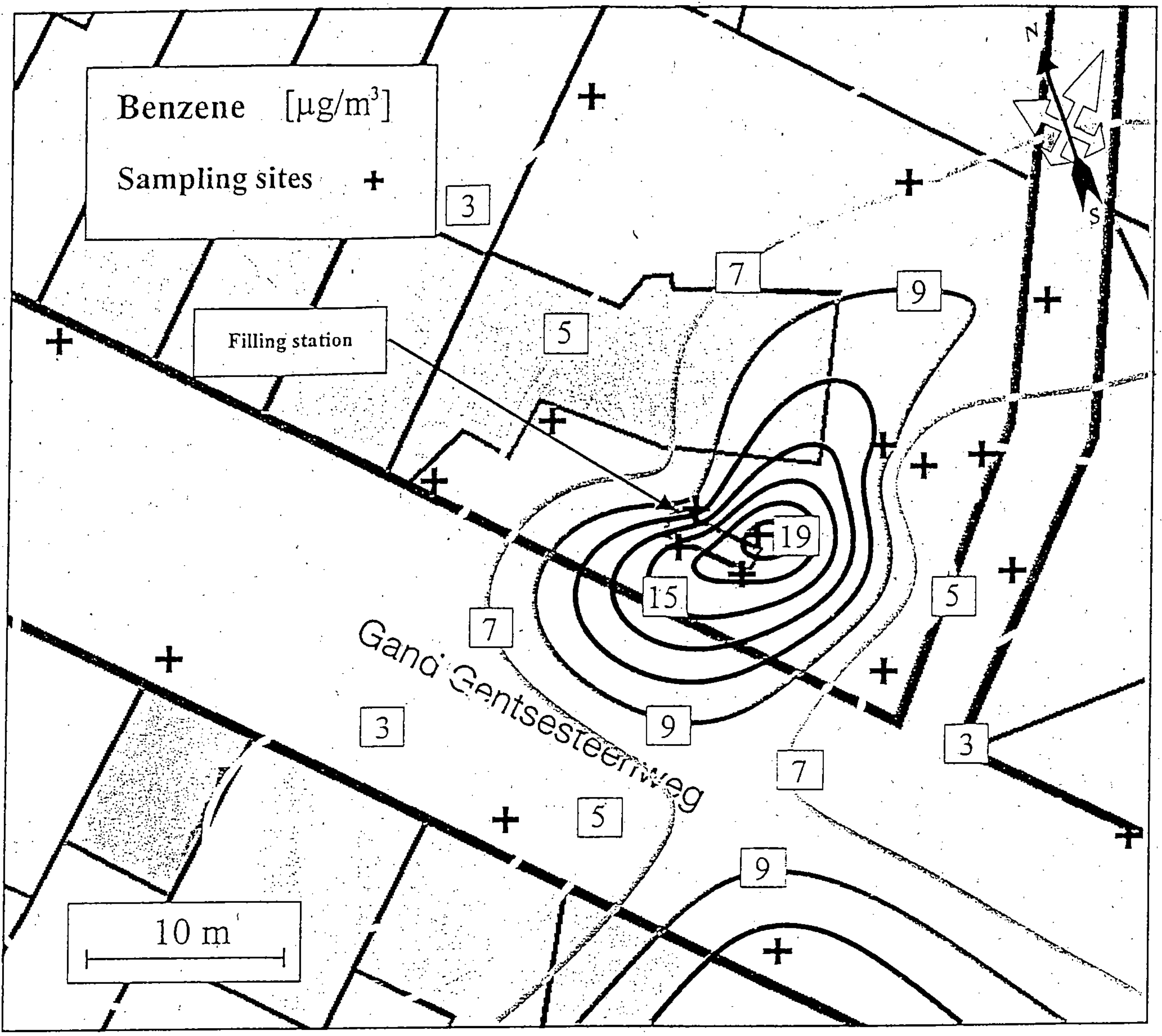
Benzene levels in petrol station C. Brussels 19/09/94 - 03/11/94



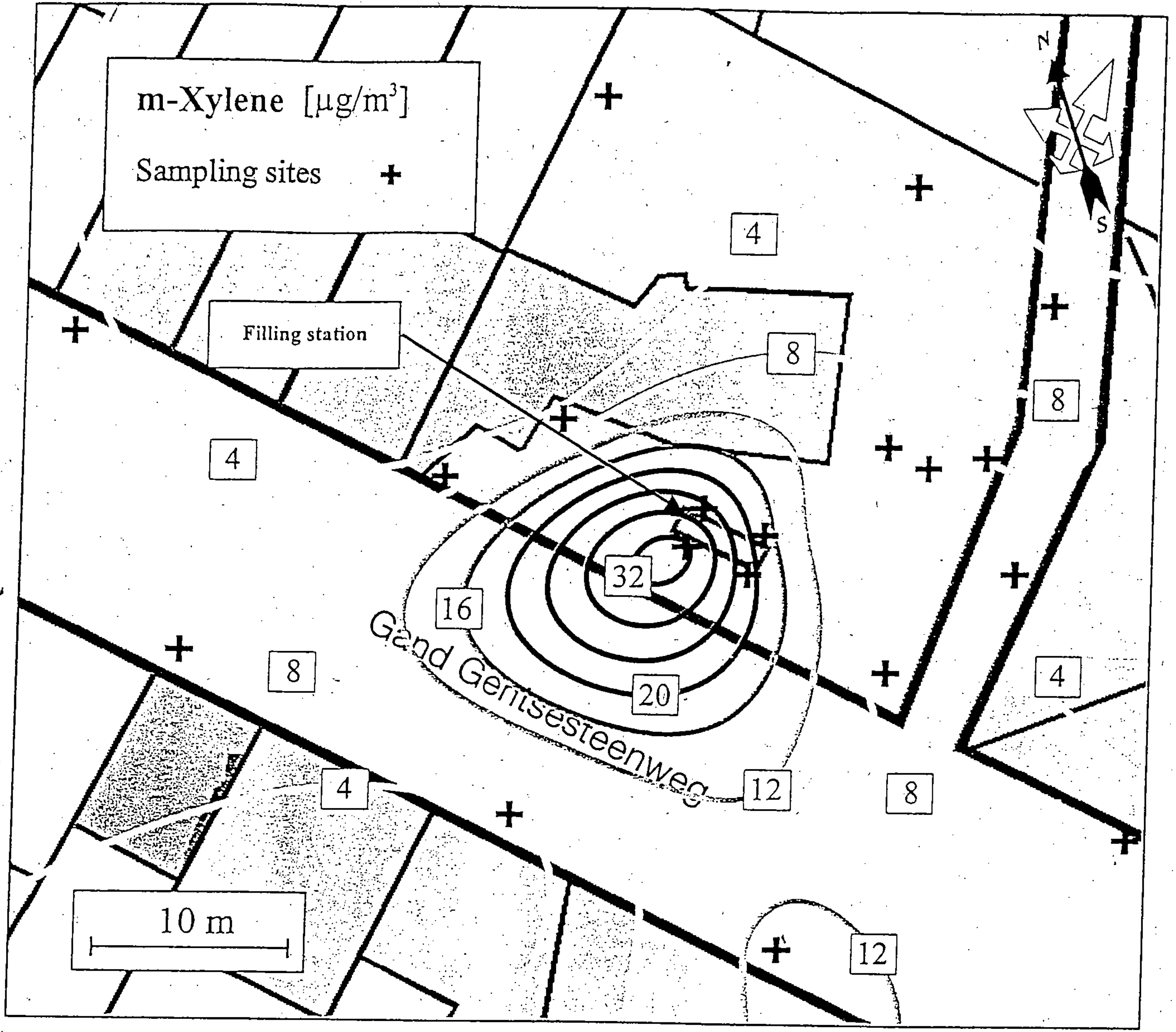
m-Xylene levels in petrol station C. Brussels 19/09/94 - 03/11/94



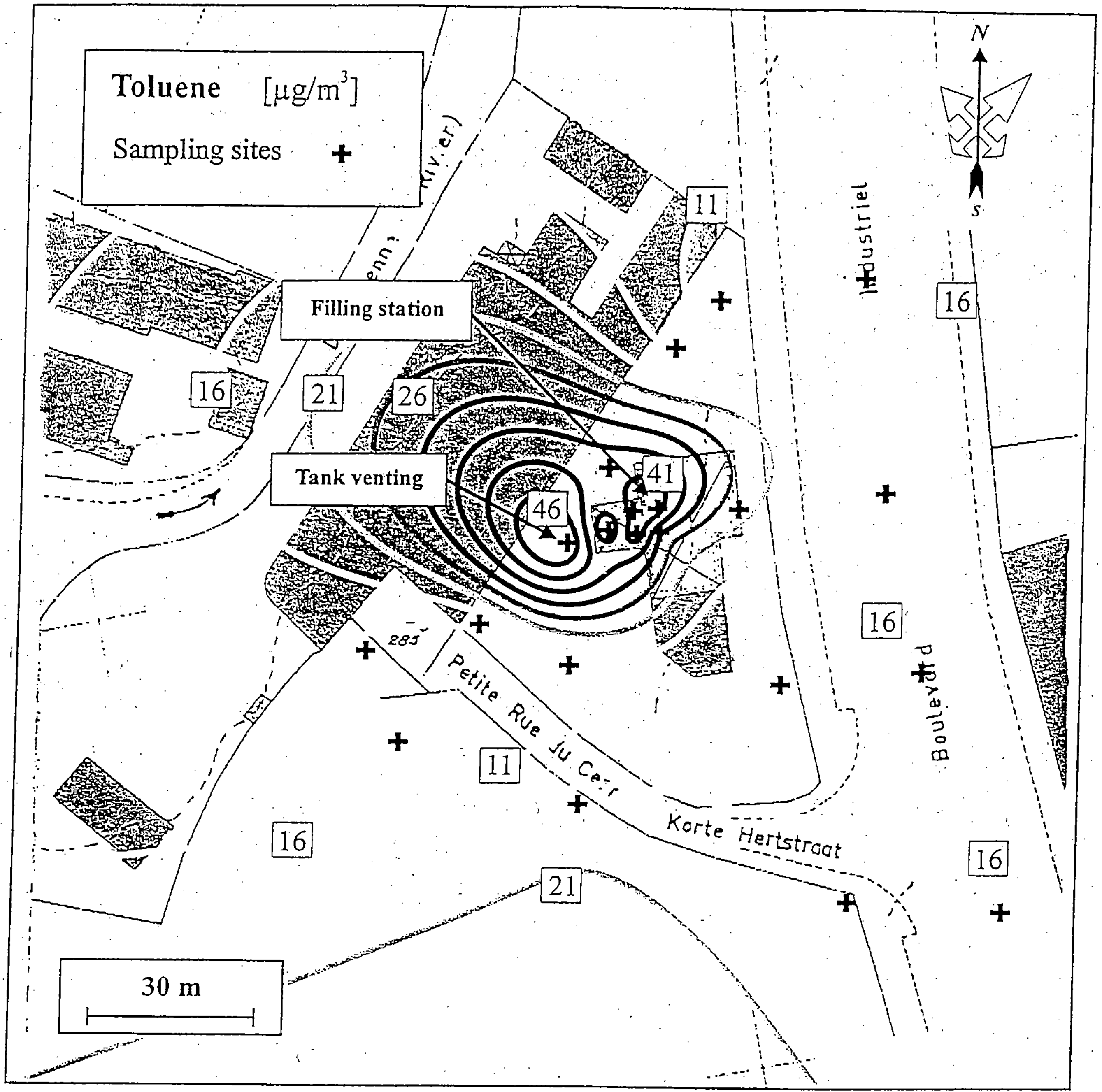
Toluene levels in petrol station D. Brussels 19/09/94 - 03/11/94



Benzene levels in petrol station C. Brussels 22/01/94 - 05/03/94



m-Xylene levels in petrol station C. Brussels 22/01/94 - 05/03/94



Toluene levels in petrol station D. Brussels 22/01/94 - 05/03/94

Annex 2

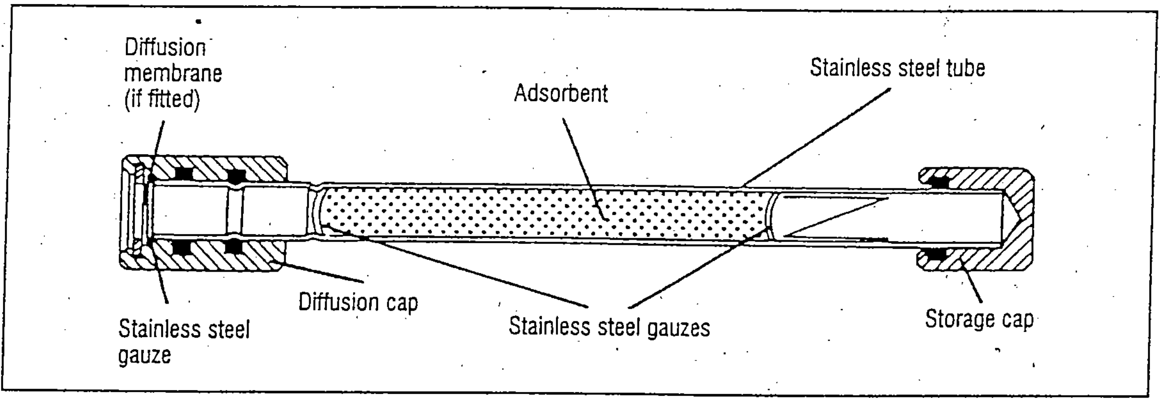
Description and mechanism the BTX diffusive sampler

Introduction

The passive sampling technique has been used for a long time in industrial hygiene as an alternative method to the active sampling for the determination of organic airborne compounds. The agreement between passive and active sampling has been widely discussed and validation protocols have been developed and standardised. Recently, the passive sampling technique has also been applied for indoor and outdoor air monitoring. The low concentrations found in ambient air require long periods of sampling, generally between two and four weeks. On the other hand, the ambient air passive samplers are exposed to variable atmospheric conditions that are quite different from the industrial hygiene environment. As a consequence, it is not possible to transfer the passive sampling validation from the industrial to the ambient environment. A new validation for ambient air passive samplers must therefore be carried out in order to establish this technique as an alternative method for detecting organic airborne compounds. Although the perspectives of this new technique are very promising, the results should be still taken from a semi-quantitative point of view.

Description of the passive sampler

Perkin Elmer passive samplers have been used in this monitoring campaign. This passive sampler (see figure below) has a tubular design where the diffusion path is followed by a long adsorbent bed. The sampler disposes of a silicone membrane, in order to reduce wind turbulence in the diffusion path and humidity effects on the adsorbent.



The length of the diffusion path is 1.5 cm with a diffusion surface of 0.2 cm^2. The length of the adsorbent layer depends on the amount of adsorbent that has been loaded. For the tubes used in this work, the adsorbent bed has a length of 6 cm.

Chromosorb 106 60/80 mesh was used as adsorbent. This is a porous polymer with a surface area between 700 and 800 m^2/g. It is considered as a class III adsorbent according to the Kiselev classification. Chromosorb 106 is a weak adsorbent, although its behaviour could be ranged between Tenax (porous polymer) and other stronger adsorbents like Carbotrap (graphitized carbon), or Carbosieve S-III (carbon molecular sieve).

Passive sampling mechanism

Because of the tubular design of this passive sampler and the fact that weak adsorbent is used, the Fick's first law can not be directly used to describe the adsorption mechanism. A no-stationary state of diffusion should be applied to model this mechanism. The Fick's second law is nor-

European Commission

EUR 16309 – Benzene, Toluene and Xylene measurements in the vicinity of petrol stations

P. Pérez Ballesta, E. De Saeger

Luxembourg: Office for Official Publications of the European Communities

1995 – 54 pp. – 21.0 x 29.7 cm

Environment and quality of life series

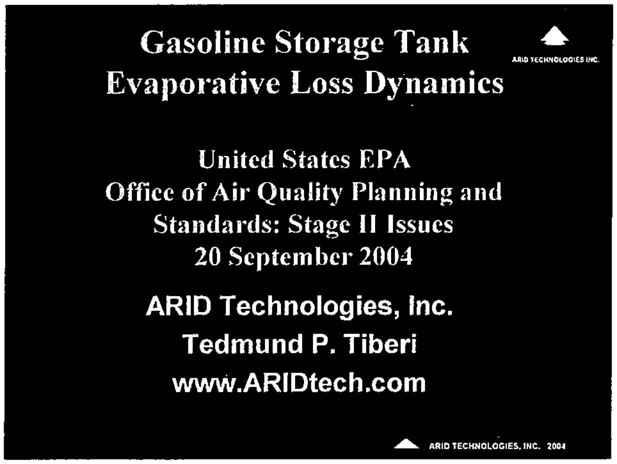
Catalogue number CL-NA-16-309-EN-C

In order to assess the impact of petrol stations on ambient VOC levels, a series of measurements has been carried out by ERLAP in the vicinity of four petrol stations in Northern and Southern Europe (Brussels and Murcia). Approximately 20 diffusive sampling sites were selected in the immediate service area and in the vicinity of each petrol stations, covering an area of approximately 200 metres in diameter. In addition, active sampling sites were selected within the boundary of the petrol station. Benzene, toluene and m-xylene concentrations were determined in this study, as the most important health-related compounds emitted by petrol stations.

The levels of hydrocarbon emissions generated by petrol stations mainly depend on factors such as the volume of fuel sales, the type and characteristics of the fuel and the meteorological conditions. The ambient temperature influences greatly the concentration of aromatic hydrocarbons in the gas phase of the fuel. A change in temperature from 5 to 35 °C leads to an increase in the concentration of benzene in the gas phase by a factor of three. In addition, wind speed and atmospheric stability influence the grade of dispersion of the emissions and consequently, the level of contamination around a petrol station. The BTX levels recorded during the measuring campaigns were approximately 5-15 times higher than the background levels, but high concentrations were only measured in the areas adjacent to the petrol station. At a distance of 100 m from the distribution pumps in Murcia and 30 m in Brussels, the levels of contamination due to evaporative emissions were negligible. As could be expected, the highest BTX concentration levels were detected in the locations and during the periods with the highest ambient temperatures. The composition of the hydrocarbons around the petrol stations changed with respect to the background, with an increasing proportion of the more volatile compounds emitted when closer to the petrol station.

The results of the study have shown that the impact of filling stations, when installed in residential areas will lead, to a systematic breaching of the proposed EU limit value for benzene (10 $\mu g/m^3$).

Appendix 6
"Gasoline Storage Tank Evaporative Loss Dynamics"
Presentation by Tedmund P. Tiberi, ARID Technologies, Inc.
US EPA, RTP
20 September 2004



Gasoline Storage Tank Evaporative Loss Dynamics

United States EPA
Office of Air Quality Planning and Standards: Stage II Issues
20 September 2004

ARID Technologies, Inc.
Tedmund P. Tiberi
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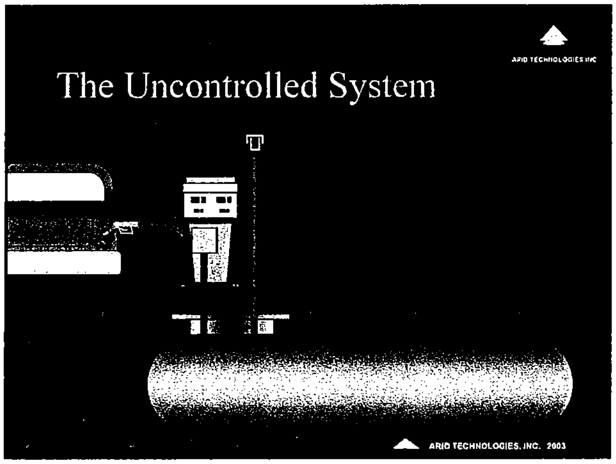
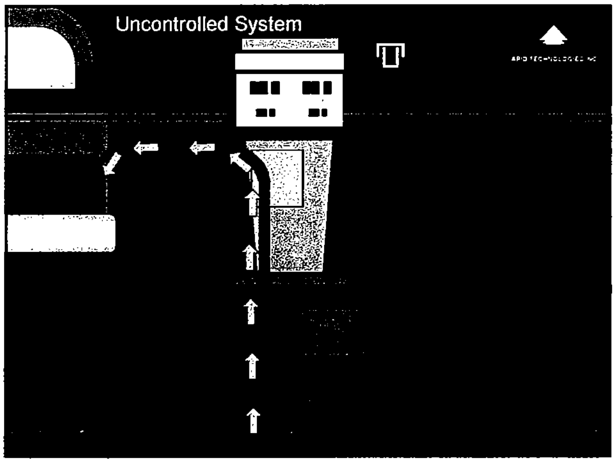


The Uncontrolled System

ARID TECHNOLOGIES INC.



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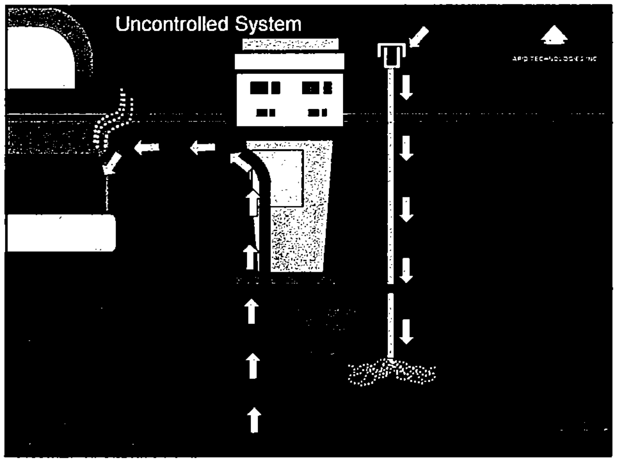

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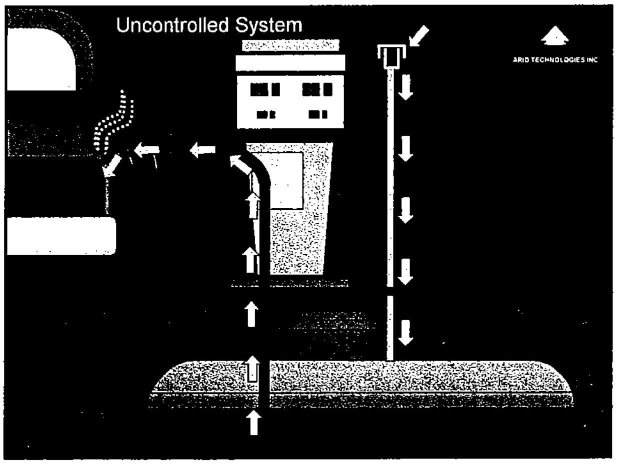

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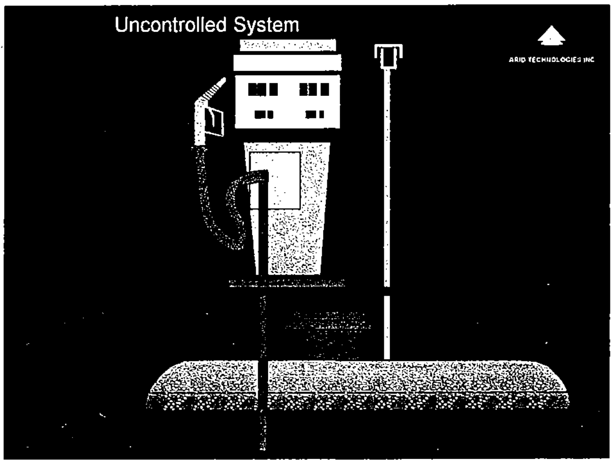

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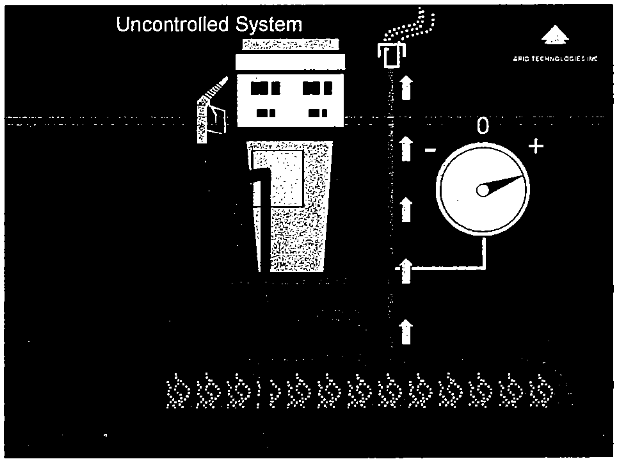

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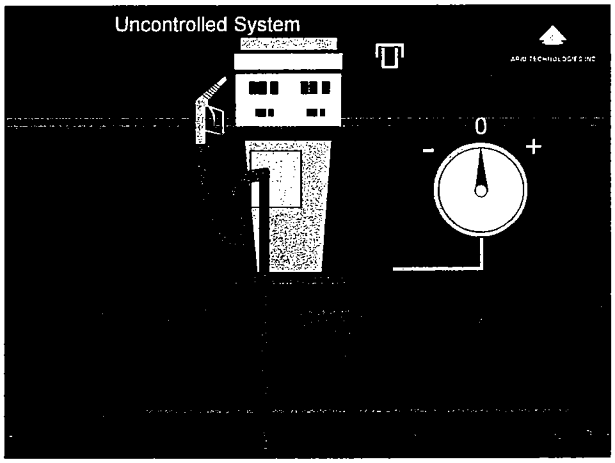
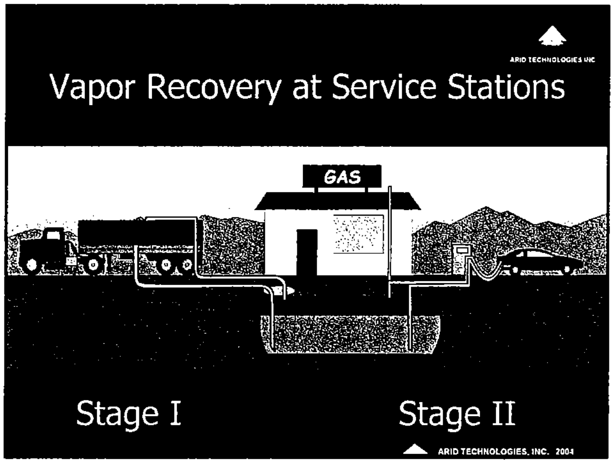


Uncontrolled System



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Vapor Recovery at Service Stations

Stage I

Stage II

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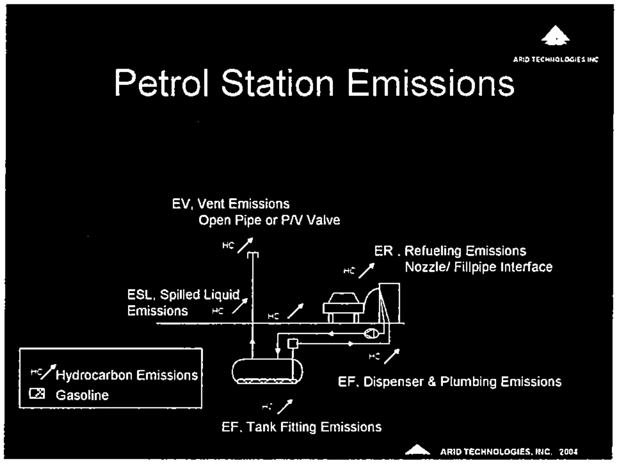

ARID TECHNOLOGIES INC

Petrol Station Emissions

EV, Vent Emissions
Open Pipe or P/V Valve

ER . Refueling Emissions
Nozzle/ Fillpipe Interface

ESL, Spilled Liquid
Emissions

EF, Dispenser & Plumbing Emissions

EF, Tank Fitting Emissions

HC Hydrocarbon Emissions
Gasoline

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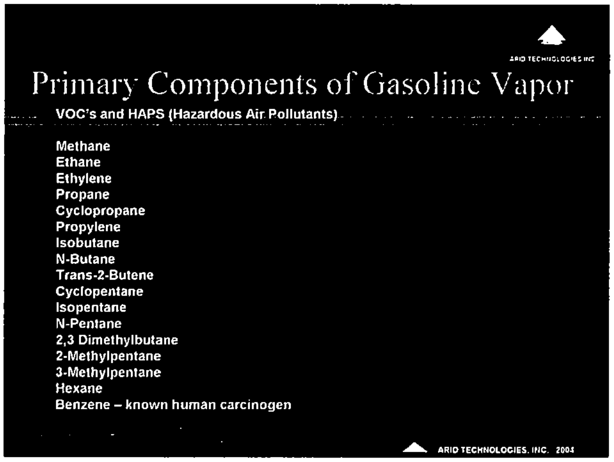

ARID TECHNOLOGIES INC

Primary Components of Gasoline Vapor

VOC's and HAPS (Hazardous Air Pollutants)

- Methane
- Ethane
- Ethylene
- Propane
- Cyclopropane
- Propylene
- Isobutane
- N-Butane
- Trans-2-Butene
- Cyclopentane
- Isopentane
- N-Pentane
- 2,3 Dimethylbutane
- 2-Methylpentane
- 3-Methylpentane
- Hexane
- Benzene – known human carcinogen

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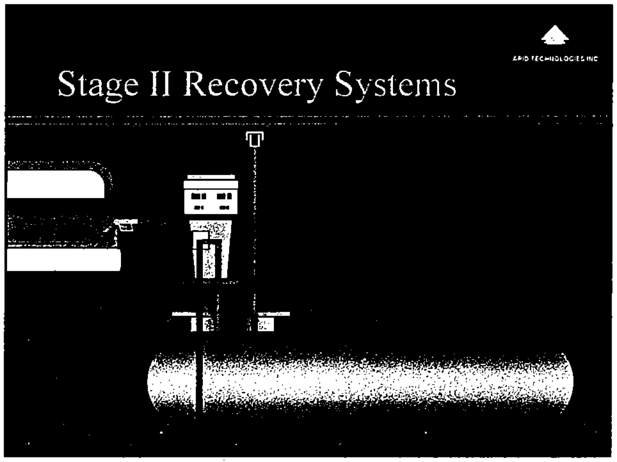

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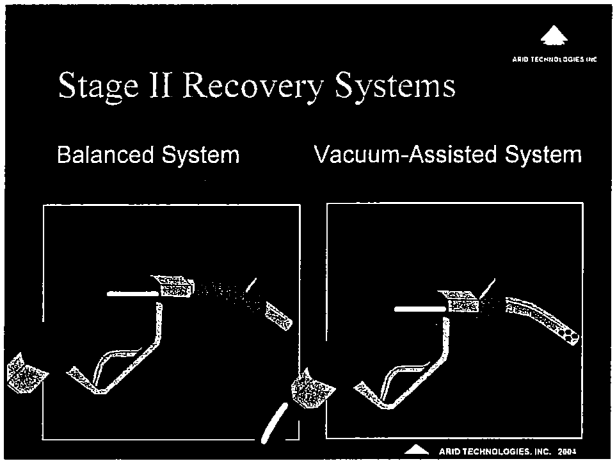
Stage II Recovery Systems



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Stage II Recovery Systems

Balanced System

Vacuum-Assisted System

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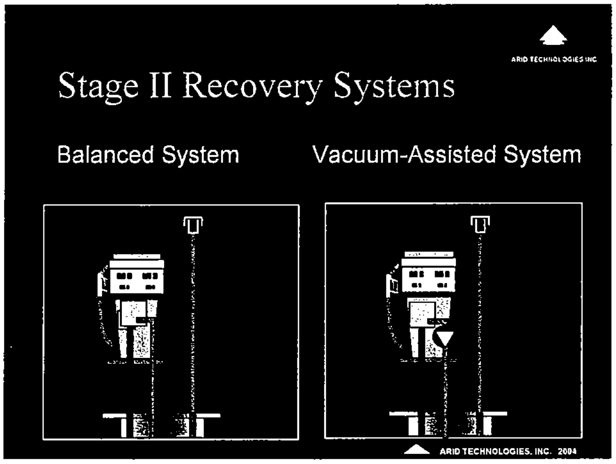

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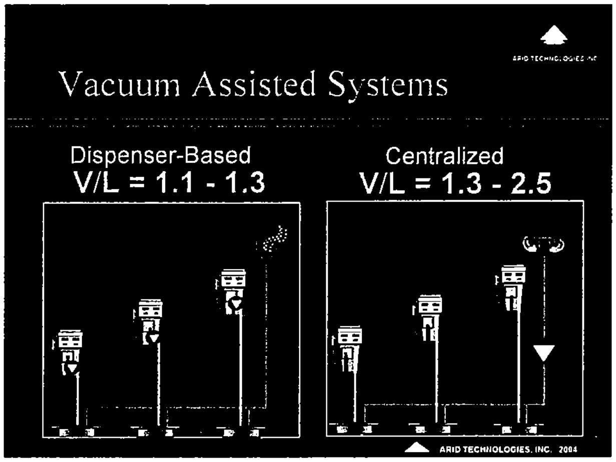
Stage II Recovery Systems

Balanced System

Vacuum-Assisted System

ARID TECHNOLOGIES, INC. 2004



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Vacuum Assisted Systems

Dispenser-Based
V/L = 1.1 - 1.3

Centralized
V/L = 1.3 - 2.5

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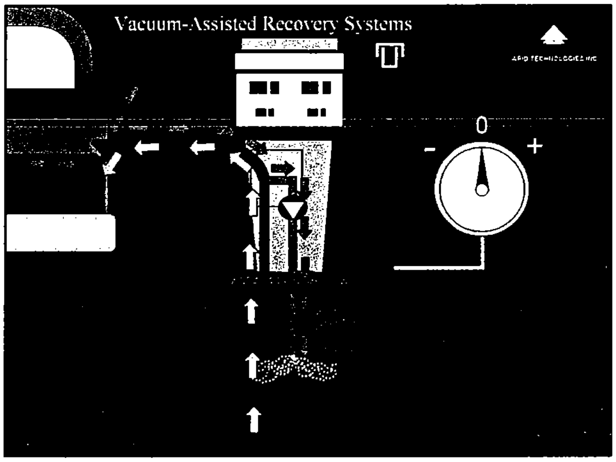
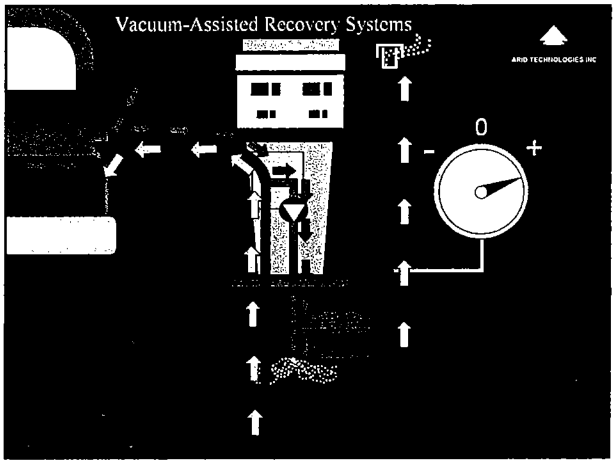
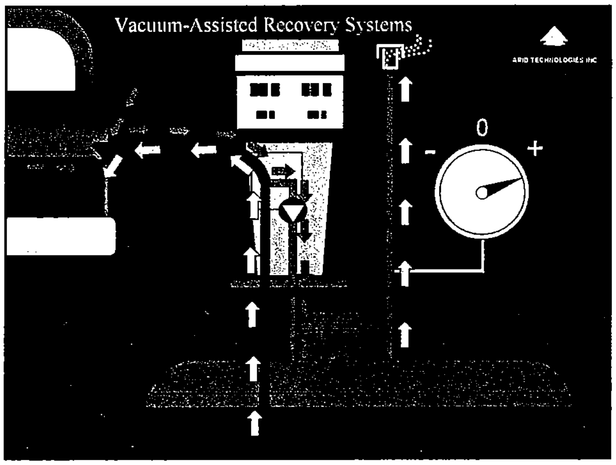


Vacuum-Assisted Recovery Systems

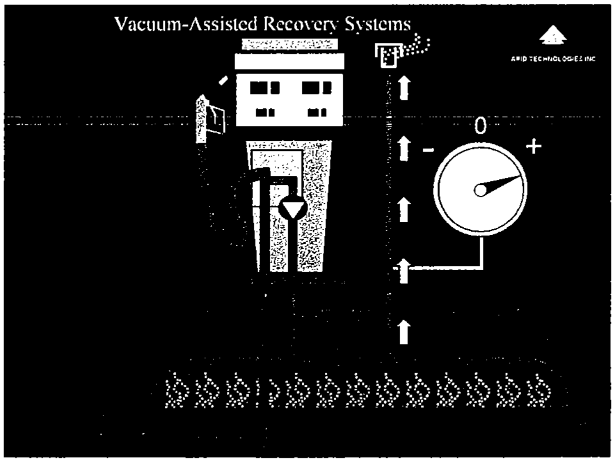
ARID TECHNOLOGIES INC



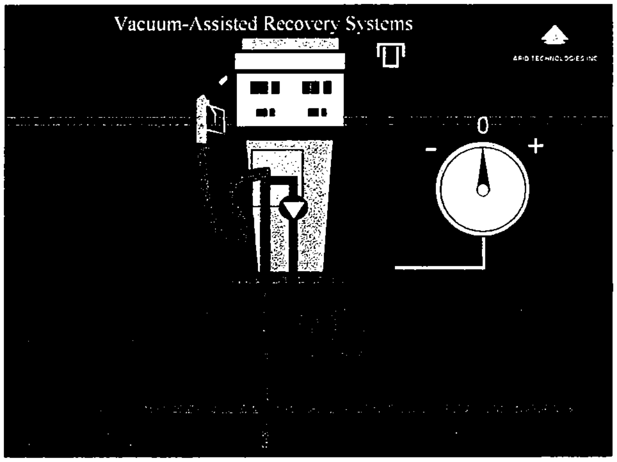
Vacuum-Assisted Recovery Systems



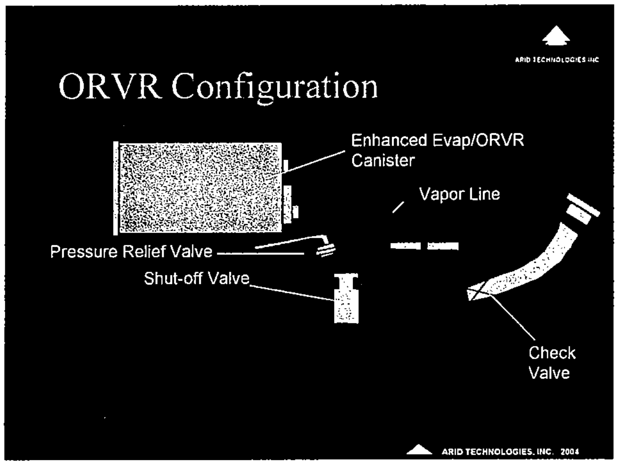
Vacuum-Assisted Recovery Systems



Vacuum-Assisted Recovery Systems



Vacuum-Assisted Recovery Systems



ORVR Configuration

Enhanced Evap/ORVR Canister

Vapor Line

Pressure Relief Valve

Shut-off Valve

Check Valve

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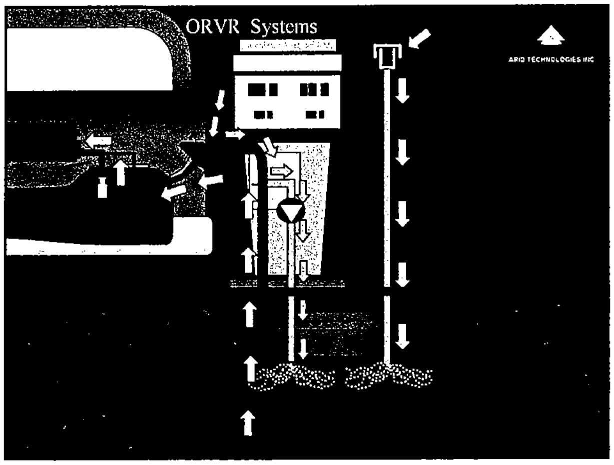
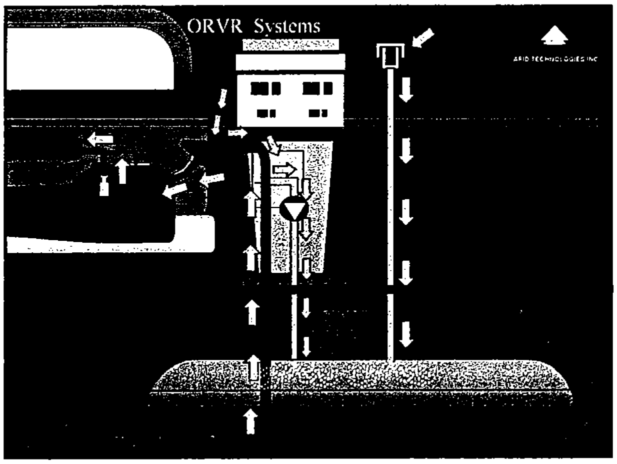
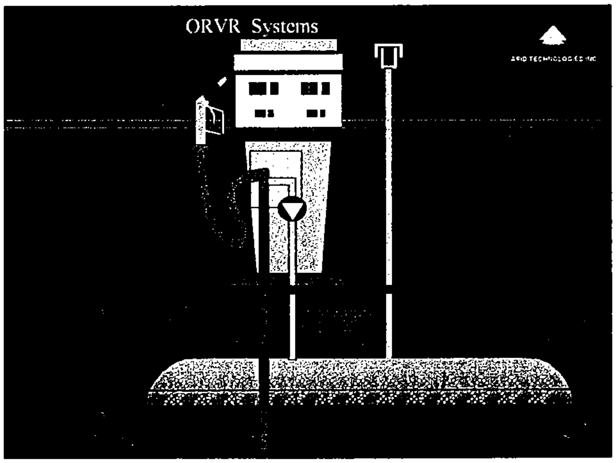


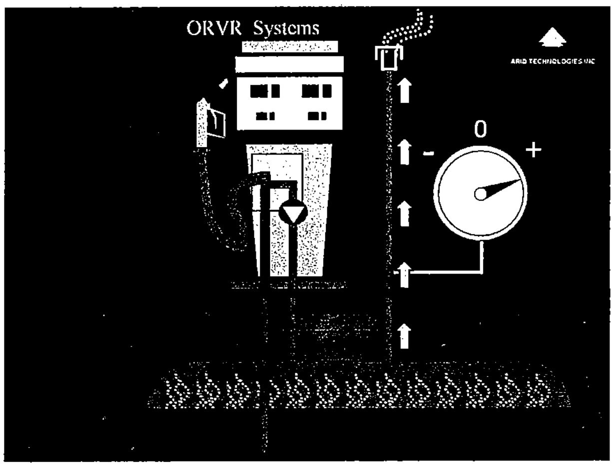
ORVR Systems



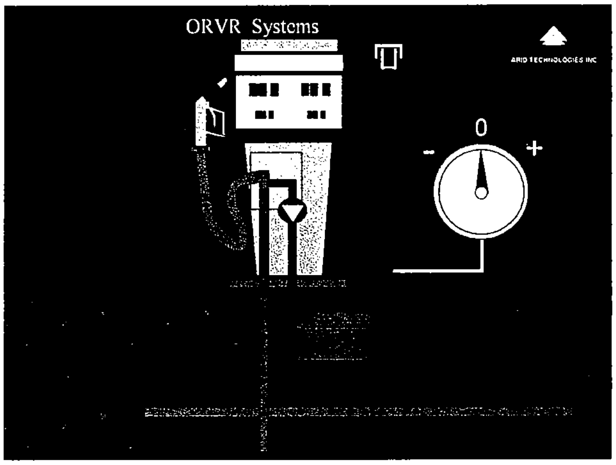
ORVR Systems



ORVR Systems



ORVR Systems



ORVR Systems

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ORVR Compatibility

- Onboard Refueling Vapor Recovery, or ORVR, provides for collection of the refueling vapors in a carbon canister on the vehicle. It performs the same function as a Stage II vapor recovery system for newer cars.
- Minimizing impact of air ingestion while refueling ORVR equipped vehicles

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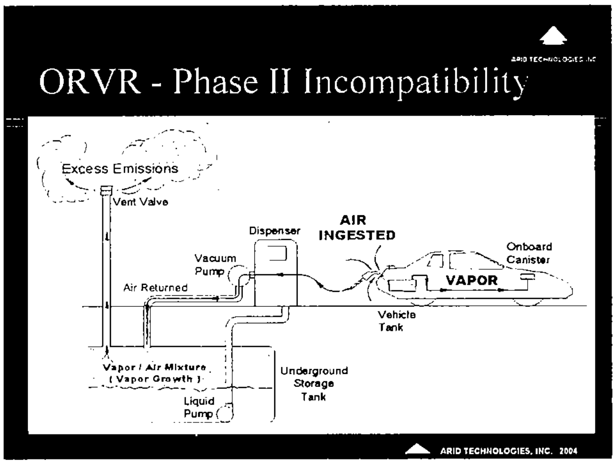
ORVR - Phase II Incompatibility



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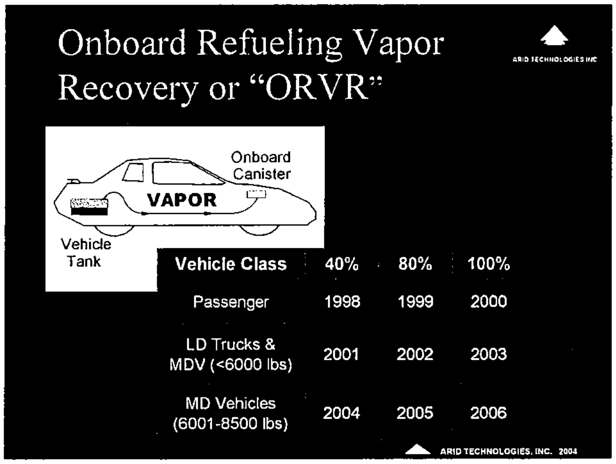

Onboard Refueling Vapor Recovery or "ORVR"

Vehicle Class	40%	80%	100%
Passenger	1998	1999	2000
LD Trucks & MDV (<6000 lbs)	2001	2002	2003
MD Vehicles (6001-8500 lbs)	2004	2005	2006

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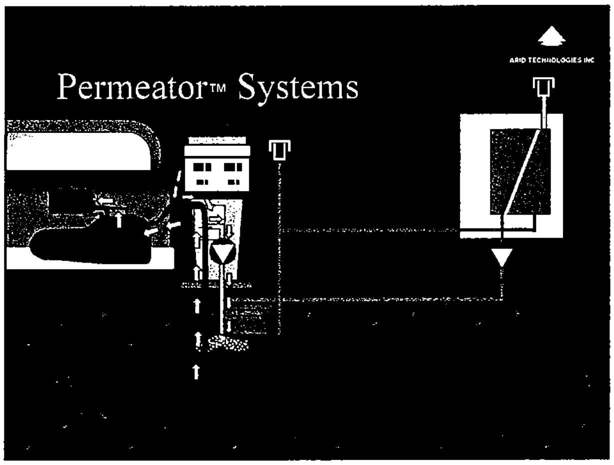
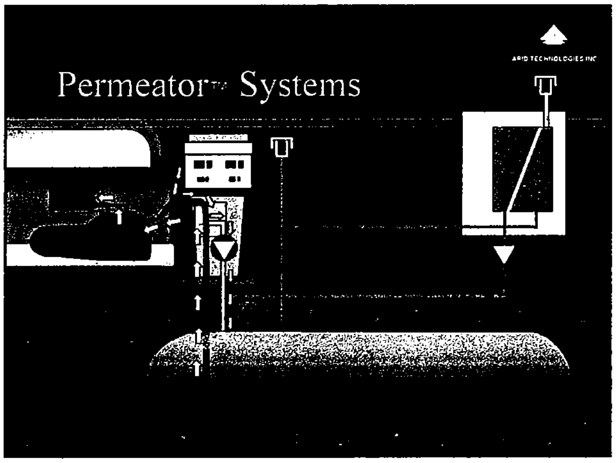
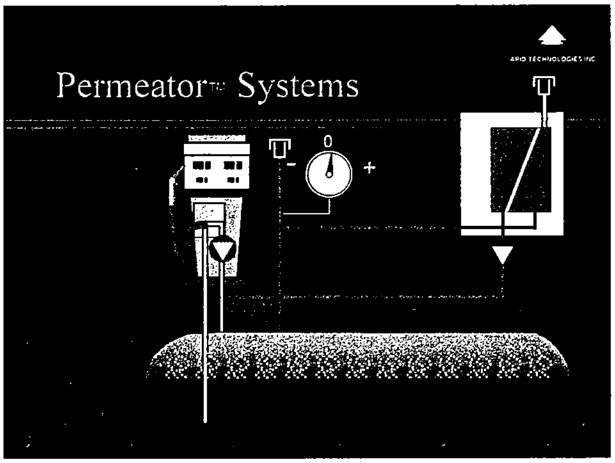


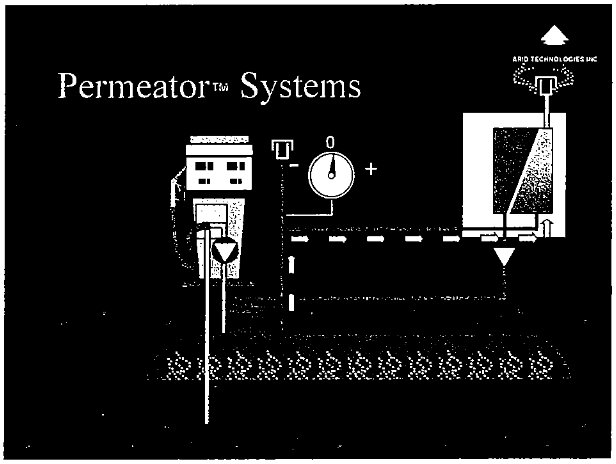
Permeator™ Systems



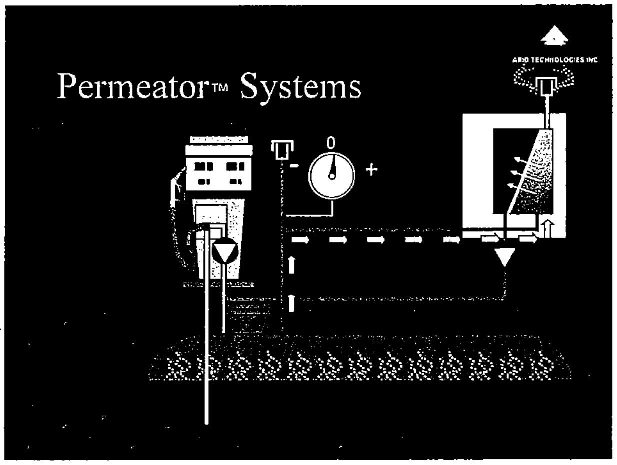
Permeator™ Systems



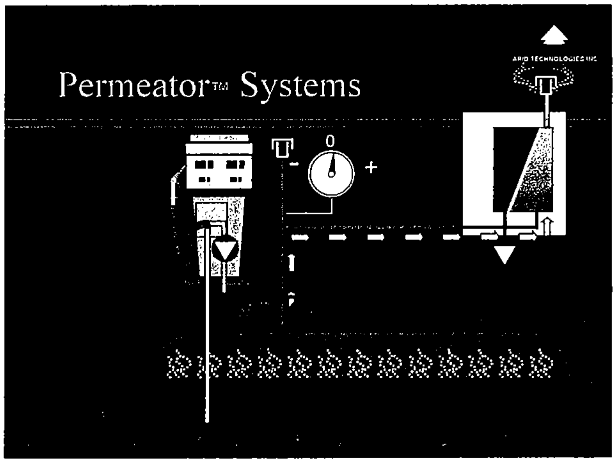
Permeator™ Systems



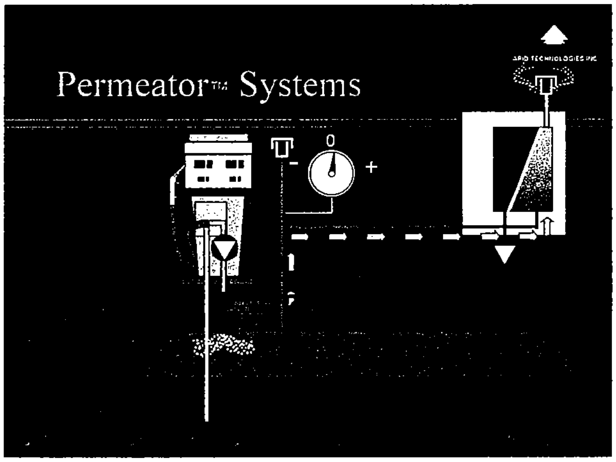
Permeator™ Systems



Permeator™ Systems



Permeator™ Systems



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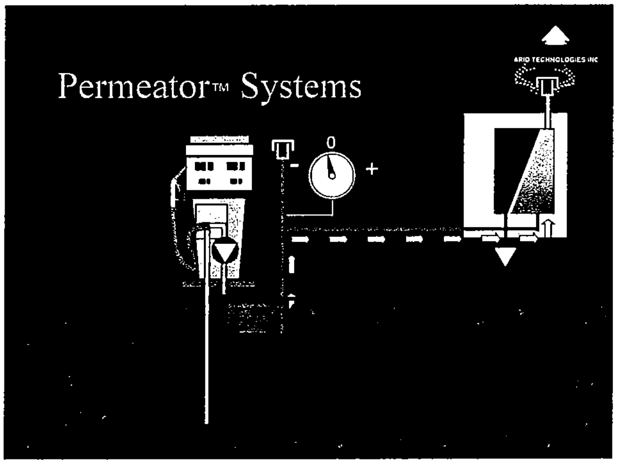

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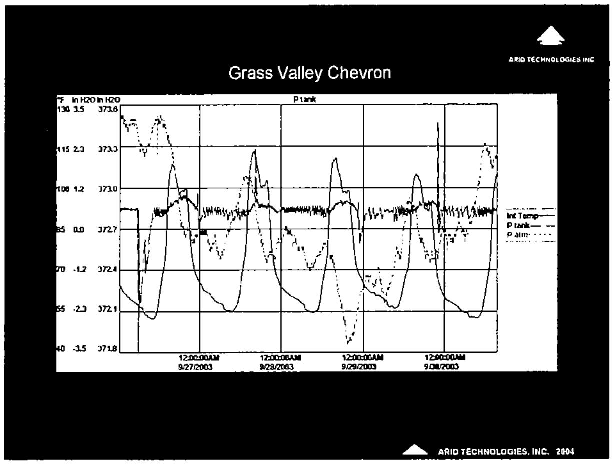
Permeator™ Systems



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Grass Valley Chevron

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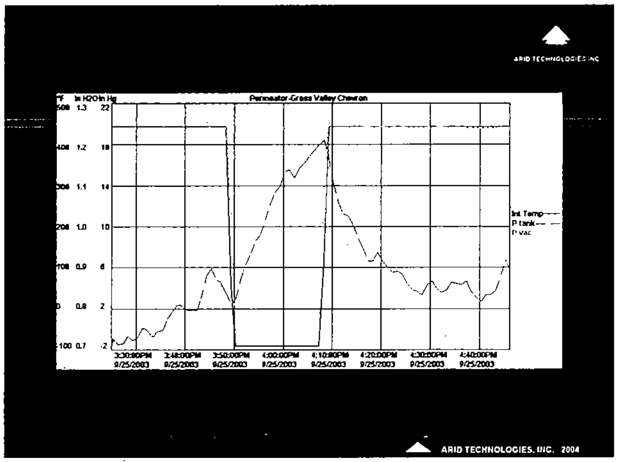

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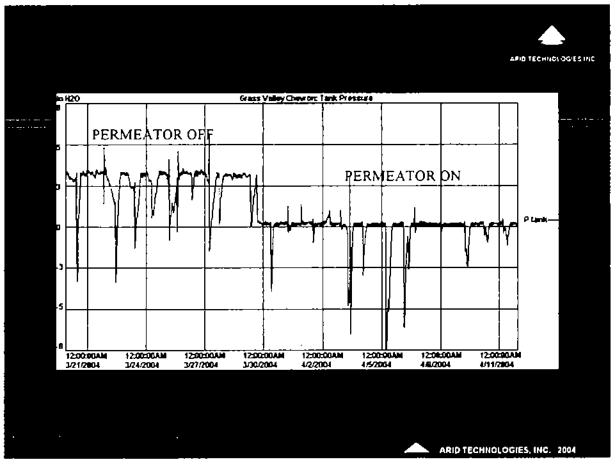

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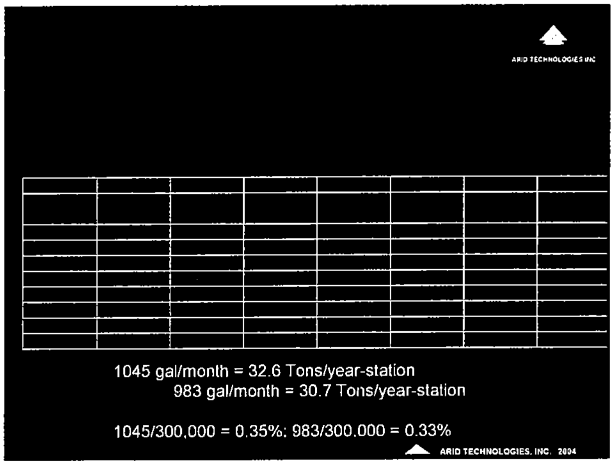
ARID TECHNOLOGIES, INC. 2004



ARID TECHNOLOGIES INC

1045 gal/month = 32.6 Tons/year-station
983 gal/month = 30.7 Tons/year-station

1045/300,000 = 0.35%: 983/300.000 = 0.33%

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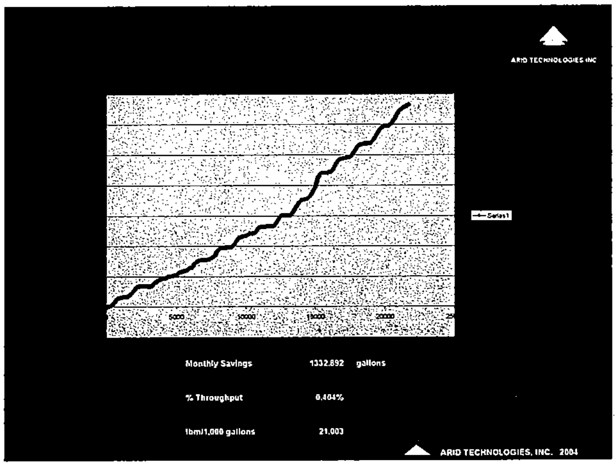

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Monthly Savings	1332.892	gallons
% Throughput	0.404%	
lbm/1,000 gallons	21.003	

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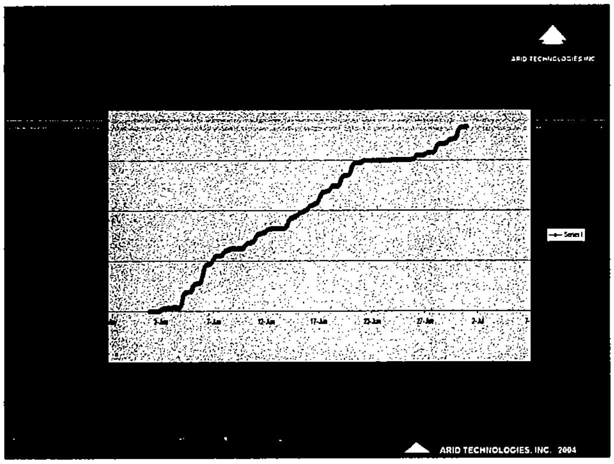

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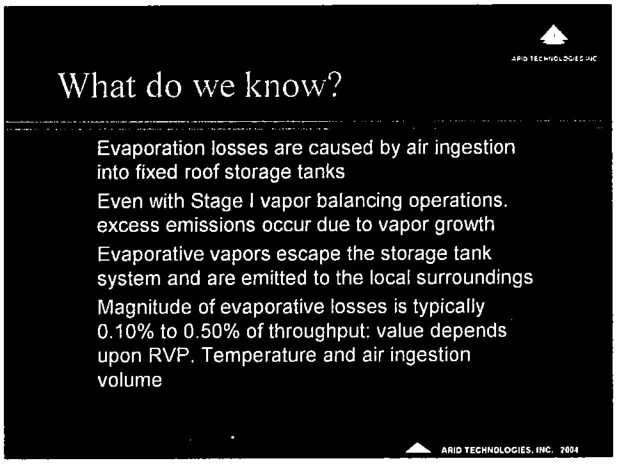

ARID TECHNOLOGIES INC

What do we know?

- Evaporation losses are caused by air ingestion into fixed roof storage tanks
- Even with Stage I vapor balancing operations. excess emissions occur due to vapor growth
- Evaporative vapors escape the storage tank system and are emitted to the local surroundings
- Magnitude of evaporative losses is typically 0.10% to 0.50% of throughput: value depends upon RVP, Temperature and air ingestion volume

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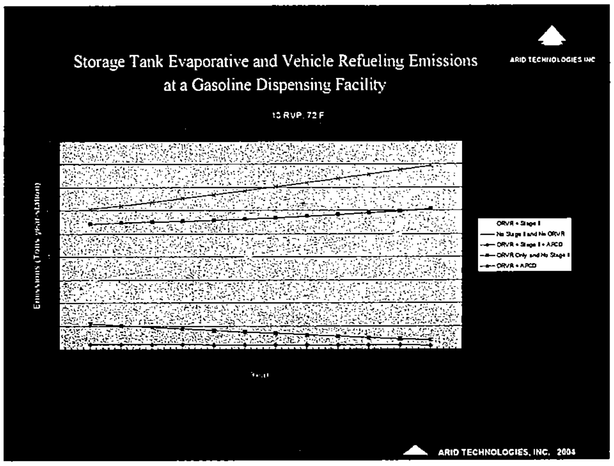

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Storage Tank Evaporative and Vehicle Refueling Emissions at a Gasoline Dispensing Facility

10 RVP, 72 F

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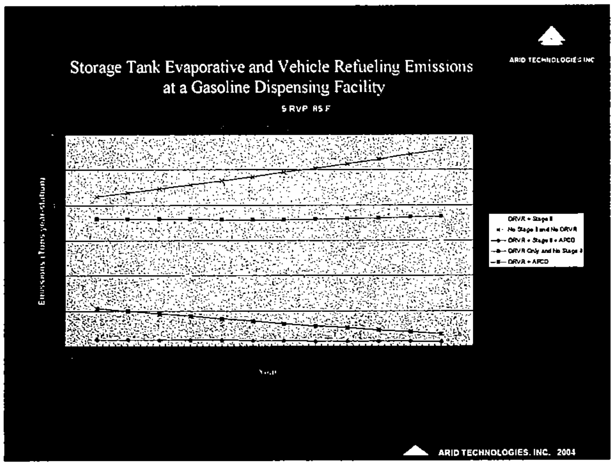

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Storage Tank Evaporative and Vehicle Refueling Emissions at a Gasoline Dispensing Facility

9 RVP, 85 F

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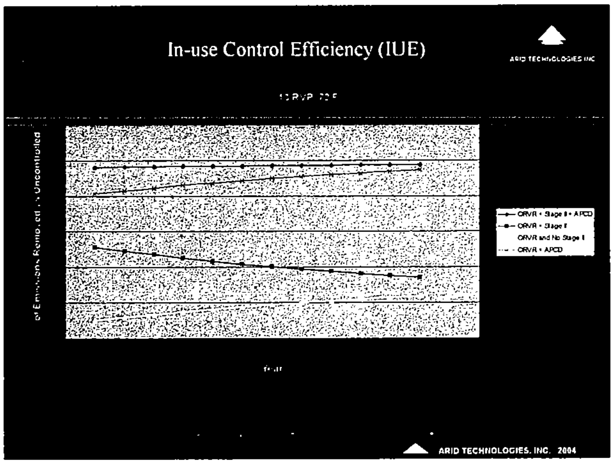

In-use Control Efficiency (IUE)

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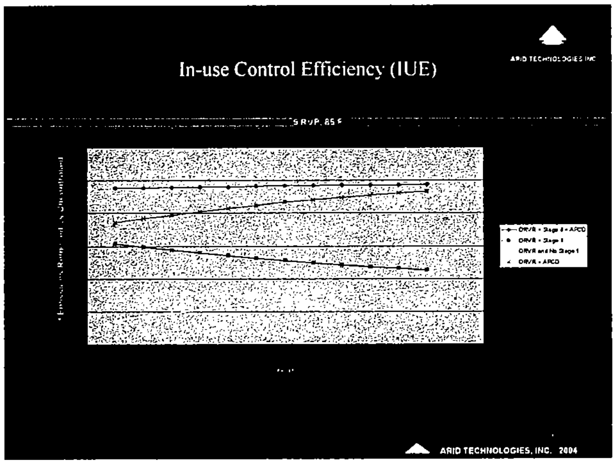
10 RVP, 72 F

ARID TECHNOLOGIES, INC. 2004



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In-use Control Efficiency (IUE)

9 RVP, 85 F

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