Risk Assessment Relating to the Potential for Contamination of the Penderyn Reservoir by Releases from the Proposed Enviroparks Site at Hirwaun

Introduction

1. Welsh Water outlined their concerns regarding the potential for the airborne releases from the proposed Enviroparks site at Hirwaun (the Hirwaun site) to impact the neighbouring Penderyn reservoir at meetings between Welsh Water and Enviroparks on 30th March and 1st April 2009. Following these meetings the dispersion and deposition over the reservoir has been modelled.

2. This note describes our method and risk assessment. This note is used as the supporting information for the completed Welsh Water risk assessment form which accompanies this note.

   Background

3. Welsh Water has requested that Enviroparks carry out a risk assessment using its own methodology for assessing the risk for potential contamination.

4. Enviroparks has taken advice from water industry and pollution experts in completing this assessment.

5. **The Concerns**

6. Drinking water for the locality is stored and supplied from the Penderyn reservoir and its associated infrastructure. Consequently it is essential that the water within the reservoir can be processed through the existing infrastructure so as to deliver water compliant with The Water Supply (Water Quality) Regulations 2000, to its customers. The chemical quality standards, potentially influenced by the Hirwaun site, are listed in Table 1 below:

Table 1

Drinking water quality standards

Pollutant	Concentration of Standard	Units of Standard
Nitrate	50	mg NO_3/l
Nitrite	0.5	mg NO_2/l
Sulphate	250	mg SO_4/l
Chloride	250	mg Cl/l
Fluoride	1.5	mg F/l
Benzene	1	µg/l
Antimony	5	µg Sb/l
Arsenic	10	µg As/l
Cadmium	5	µg Cd/l
Chromium	50	µg Cr/l
Copper	2	mg Cu/l
Lead	10 (as of 25 December 2013)	µg Pb/l
Manganese	50	µg Mn/l
Mercury	1	µg Hg/l
Nickel	20	µg Ni/l

Environmental Management at the Hirwaun Site

7. The direct environmental releases at the proposed Enviropark's site at Hirwaun will be to air, arising from the engine exhausts. The only additional releases are transitional releases, such as from flares which are used for situations including emergency conditions and the start up and shut down of various plant items. By their nature these are short term releases. The release is necessary for effective health

and safety management and they will be via “state of the art” flare systems. They cannot be effectively modelled.

8. The engines are designed, managed and abated so as to discharge into one of the site stacks which are 40 m high. The dispersion from the stacks has been designed to ensure the site complies with all relevant short and long term air quality standards. The ADMS dispersion model was used to predict the likely effects of these releases. NO_x was the dominant air quality release of concern.

9. The site’s operation and dispersion have been engineered so as to ensure that the predicted environmental concentration (PEC) of NO_x remains within 70 % of the Air Quality Objective (AQO) for NO_2. That is, the sum of the background concentration of NO_2 and the process contribution of NO_x remains within 70 % of the AQO and can therefore be considered to be acceptable to the air quality standards, and not requiring any further study. The PEC for other pollutants was less and was generally considerably lower than 70 % of the relevant standard.

10. The ethos of emissions management at the Hirwaun site is to avoid and, where unavoidable, control issues from the start of the process, abating the problems at the earliest effective opportunity. As such we seek to monitor and control potential pollutants on site so as to prevent harm rather than abate at the end of the process and monitor beyond the site to look for the absence of harm.

The fuels to be used at Hirwuan

11. Initially three fuels will be used to fuel individual engines at Hirwuan. The planning application includes the use of a fourth fuel, syngas; this is likely to come on line after the first three. The fuels are:

    - Biogas: a simple mixture of almost entirely methane and carbon dioxide. The burning characteristics in the engine are similar to natural gas. Exhausts are clean by industry standards, metal pollutants are effectively non existent and VOC releases, with a carbon number greater than 1 are very low. Historically methane releases have been relatively high from such engines, this presents a global warming challenge rather than an air quality issue.

    - Pyrogas: Pyrogas is a complex mixture of carbon oxides, hydrogen, water and a range of VOCs. The Enviroparks pyrolysers are high temperature units, which favours the formation of low MW VOC. In addition the pyrogas is scrubbed prior to use to remove high molecular weight materials including tars. As a result the pyrogas composition effectively has a molecular weight cut off equating to about C7. It could be claimed that combustion is not dissimilar to that of petrol; an additional benefit of pyrogas is that it is fed as a gas into the engine and not as a vaporising liquid. Metal contamination of the gas will be as low as petrol but without any additives, very low.

- Tallow: This is a mixture of free fatty acids together with mono, di and tri glycerides. Enviroparks process produces tallow with a low contamination with materials such as carbohydrate and protein. The tallow will be burnt in a compression ignition engine, the tallow being injected during the power stroke. Clearly the tallow will have to be filtered to a very fine level to prevent the wear of the injectors and pumps; as a result metal contamination is likely to be very low.

- The final and future fuel is syngas: This is a simple mixture of carbon oxides, hydrogen and water. The only VOC present is likely to be a small quantity of methane, formed by the Sabatier reaction. Whilst this is a low calorific value gas it is expected to give a clean burn, in terms of VOC formation in the exhaust. Again the final gas cleaning system incorporates both filtration, including carbon, and a relatively low temperature. As a result metal carryover will be low.

12. As a result from the above description variations in the precise inputs to the site are not likely to influence the composition of releases from the site. What needs to be considered is disturbances or variations in the releases to air arising from the engines or in the event of their failure from the flares.

The issue to be considered: short term or long term releases

13. There are essentially only two operating states for the site that need to be considered:

    - Routine operation, long term releases; and
    - Transient conditions, eg. Flaring, short term releases

    These are considered below:

14. The reservoir is a large volume of water and the Hirwuan site is a small but potentially steady releaser of various potential pollutants. It is unlikely that transient releases from the site pose a significant risk to the quality of the reservoir. A sensitivity analysis is shown in Table 2 below. This assumes that the *maximum possible permitted site release rate of each pollutant (at the air quality standard) is directly dissolved into the reservoir.* This is a practical impossibility in that it does not take into account any external factors such as air dispersion or any reduced rate of absorption created by boundary conditions between air and water.

15. It then calculates the number of hours that this *grossly exaggerated* release would need to continue to raise the reservoir concentration to the drinking water limit.

Table 2 – **THEORETICAL TOTAL EMISSIONS CAPTURE**

Pollutant	Kg needed to exceed standard	Release rate Maximum gr/s	Time to meet limit hr
Nitrate	30,000	19.83	420
Nitrite	300	14.71	5.7
Sulphate	150,000	6.61	6,304
Chloride	150,000	0.31	134,409
Fluoride	900	0.031	8,065
Benzene	1	0.77	0.22
Antimony	3	0.0155	54
Arsenic	6	0.0155	108
Cadmium	3	0.00155	538
Chromium	30	0.00155	5,376
Copper	1,200	0.00155	215,054
Lead	6	0.0155	108
Manganese	30	0.0155	538
Mercury	1	0.00155	108
Nickel	12	0.0155	215

16. Given the extent of the pessimism used in this analysis the only releases worthy of any consideration are those for benzene and nitrite.

The likely duration of a transient release

17. Biogas is generated in two distinct AD systems. Both use a modified AD process whose details remain confidential. A benefit of this process is that the digesters operate at a very short residence time, measured in hours as compared to the conventional 15 to 25 days. An advantage is that in the event of a major operation problem such as catastrophic engine failure, the normal routine would be to stop or dramatically reduce the feed to the digester and divert gas to the flare. The rate of these flaring operations are likely to reduce at an exponential rate, the difference is that the half life of this decay is likely to be of the order of an hour or two rather than the more conventional several days. This dramatically reduces the potential for any adverse impact from flaring operations.

18. The pyrolysers: As with the biogas the pyrogas is generated and burnt in the engines. Should an engine fail and the remaining operating engines prove unable to consume the additional gas then it will need to be flared. The pyrolysers have an exceptionally short residence time and gas production typically ceases within 20 seconds of stopping the feed. As a result the flare duration is likely to equate to this and so is not an issue. A gas blockage within the pyrolyser may lead to a rupture of

the bursting disc with a direct vent of pyrogas, The intention is to direct these potential releases to a flare, the key issue here is safety and the full detailed engineering of this cannot be done without use of the resource that comes available after planning has been granted. Suffice to say the issue of benzene release and its consequences from this event will be considered.

19. Tallow; this is a stored fuel produced on site, there are no flares or other emergency releases associated with the use of this fuel.

Design of the flares to be used

20. All on site flares are likely to be of the enclosed flame design. At full rate they will be designed to exceed the normal requirement of 1,000 ^{0}C for 0.3 seconds. Under these conditions and the excess of oxygen gross exceedence of the VOC release and that for benzene is difficult to foresee. NO$_x$ formation under these conditions is certainly feasible but should tend towards forming Nitrogen dioxide. The NO$_x$ concentration may be higher than normal but not so dramatic as to raise a problem. Given that the flares are short term releases and at up to 1000 ^{0}C then the dispersion is likely to be greatly enhanced by the thermal lift and modelling of such a transient event is likely to be very subjective.

Consideration of the short term release of benzene

21. The analysis shown in Table 2 assumes all the VOC is benzene. This is not he case because normally benzene is typically 1 % of the total VOC, inferring that the time to meet the limit is now increased to 22 hours, assuming *no dispersion and total solubility* of the total benzene release into the reservoir. This theoretical release of Benzene cannot be maintained for 22 hours. This statement is made with the assumption that the emergency pressure relieving of the pyrolysers will be via a flare. If this does not prove to be practical at the detailed design stage then the dispersion of benzene from the pressure relief stack will be considered.

Consideration of the short term release of Nitrogen Oxide

22. None of the scenarios above indicate that the likely short term releases of nitrogen Oxide are likely to result in an exceedance of the relevant limits.

23. Should the nitrite level be exceeded it is believed that this should rapidly oxidise to nitrate so long as the oxygen tension within the reservoir is maintained at a healthy level throughout its volume. This assumption is the reason for reducing the Residual Impact score in the attached assessment.

Consideration of the long term releases

Proposed methodology

24. The site has been designed and modelled in the first instance to comfortably operate within the air quality limits as previously explained. Our approach is to check what if any additional controls are needed to ensure an insignificant impact on the reservoir.

25. By using the air quality standards to assess which releases could have a significant negative impact on water quality, we have assumed that the surface of the reservoir was continually exposed to air polluted to the air quality standards. This is *clearly not the case but is a worst case scenario*, possibly over stated by more than an order of magnitude. This is referred to as the primary assessment filter.

26. Substances not showing insignificance at the primary assessment filter are then more closely examined with respect to the actual Hirwaun site operations. This is referred to as the secondary assessment filter.

27. Substances which continue to appear significant at the secondary filter stage are then re considered through the entire process design to address and identify the cause of the problem. Methods for further release reduction can then be identified. Following this the secondary assessment is repeated.

PRIMARY ASSESSMENT FILTER

Method

28. It is assumed that the air concentrations immediately above the reservoir are continuously at the relevant air quality standard. These are shown for all substances that are a precursor to a substance with a water quality standard in Table 3. As we are considering the transfer of a small quantity of pollutant into a large mass of water then the rate of concentration change can only be very slow. Consequently it is proposed that the annual average air quality standards are appropriate for consideration, where these are available.

29. We have heeded a comment made at the meetings with Welsh Water that suggested there may be some stagnant areas of the reservoir which could mean significant areas of the reservoir have a residence time measured in years as opposed to the mean residence time of 40 days.

30. We were also asked to consider the effect of drought conditions. The lowest level recorded in the reservoir is believed to be 30%. Clearly as the reservoir volume reduces so does its capacity to dilute the pollutants. In practice drought conditions normally support good air dispersion conditions, such as still clear days allowing the plume to rise high into the air, and consequently the site plume is unlikely to be incident on the reservoir at these times. In a drought the site stack and the reservoir are likely to work in a synergistic rather than an antagonistic manner. For the reasons above we feel that an accumulation period of 5 years is a safe but realistic guideline to use, to cover any of the worst case scenarios in a single assessment.

Table 3 Air quality standards

Pollutant	**Averaging Period**	**Concentration* µg/m^3**
Nitrogen Dioxide	Annual	40
Sulphur Dioxide	Annual	20
Hydrogen Chloride	Long Term	20
Hydrogen Fluoride	Short Term	250
Benzene	Annual	5 (as of 31 December 2013)
Antimony	Long Term	5
Arsenic	Long Term	0.006
Cadmium	Annual	0.005
Chromium	Long Term	0.1
Copper	Long Term	10
Lead	Annual	0.25
Manganese	Long Term	1
Mercury	Long Term	0.25
Nickel	Annual	0.02

Notes:

- The air quality standards detailed are a combination of Air Quality Objectives, National Objectives for the protection of vegetation and Environmental Assessment Levels.

31. In our calculations we have assumed all our NO_x is NO_2 and have then sought to comply with a self imposed limit of less than the 40 µg/m^3. In practice the bulk of our NO_x is NO, and this ensures our modelling is robust. In this analysis we have assumed that the 40µg/m^3 of NO_x is simultaneously both NO and NO_2 and so leads to respectively nitrite and nitrate formation in the reservoir. Again this is plainly an overestimate of the situation. Our opinion is that nitrite, if formed, will tend to oxidise to nitrate in the reservoir assuming the water remains oxygenated.

32. SO_x in our calculations are assumed to be all SO_2, and this is likely to be close to reality. In this analysis we will assume that SO_2 dissolves so as to form Sulphate. This is a two stage reaction where sulphurous, SO_3 ions are first formed, these then oxidise to sulphate within the reservoir. Again this is adopted so as to provide a robust and worst case assessment.

33. HF is included in the analysis but a long term air quality standard is not offered. Operating at such a high concentration of HF is not possible for the plant, as the corrosion would be intolerable. It is proposed to copy the 20 µg limit for chloride for fluoride. However there is no way the fluoride concentration will equal or exceed the chloride, and hence the assessment can still be considered to be robust.

34. With these concentrations incident on the reservoir surface, an assumption has to be made as to the deposition rate of these concentrations into the reservoir. The ADMS model includes deposition factors for NO_x, SO_x and HCl only, for the species considered. These factors are also quoted for various land cover, such as short grassland and woodland, but not water. We were surprised to be unable to find relevant deposition rates from air onto water. It seems such a fundamental piece of environmental management and modelling data that by now we would expect some official organisation would have independently assessed and published this information. We have modelled the deposition of pollutants using the limited ADMS factors which we have expanded by referring to HF as a reactive specie, whilst all other species, Benzene and the metals, have been considered as un-reactive. Reactive species undergo significant chemical reaction on contact with the surface, whilst un-reactive species do not.

35. The accumulation model has been constructed and this can model both the Penderyn reservoir and its associated service reservoir.

36. The service reservoir has also been modelled. The assumption is that 5,000 m^3 of water drains out and 5,000 m^3 of air polluted to the air quality limits is drawn into the service reservoir. When the service reservoir is re flooded with water it is assumed that all of the pollutants are totally dissolved in the water (*an impossibility, as previously described*). The two assumptions are combined so as to calculate how many years the water can reside in the reservoir before the Water quality objective is exceeded. The combined results are shown in Table 4 below:

Table 4

Accumulation model results

Pollutant	Standard mg/lt	Conc rise in transfer mg/lt (Annual)	Conc rise/yr storage mg/lt	Years storage to exceed limit	Less than 5 yr standard?
Nitrate	50	5.39E-05	3.63E-01	137.76	No
Nitrite	0.5	4.00E-05	2.69E-01	1.86	Yes
Sulphate	250	3.00E-05	1.26E+00	198.05	No
Chloride	250	1.95E-05	2.05E+00	122.18	No
Fluoride	1.5	2.38E-04	1.68E+00	0.89	Yes
Benzene	0.001	5.00E-06	2.06E-02	0.05	Yes
Cadmium	0.005	5.00E-09	2.06E-05	242.41	No
Mercury	0.001	2.50E-07	1.03E-03	0.97	Yes
Lead	0.01	2.50E-07	1.03E-03	9.70	No
Arsenic	0.01	6.00E-09	2.48E-05	404.02	No
Antimony	0.005	5.00E-06	2.06E-02	0.24	Yes
Chromium	0.05	1.00E-07	4.13E-04	121.21	No
Copper	2	1.00E-05	4.13E-02	48.48	No
Manganese	0.05	1.00E-06	4.13E-03	12.12	No
Nickel	0.02	2.00E-08	8.25E-05	242.41	No

Results of the primary assessment filter

37. Adoption of the logic proposed so far states that, excedence of the water quality standards as a result of activity on the Hirwaun site should be discounted for:

Nitrate

Sulphate

Chlorine

Cadmium

Lead

Arsenic

Chromium

Copper

Manganese

Nickel

38. The sources and effects of the following should be considered at the Secondary assessment filter:

Nitrite

Fluoride

Benzene

Mercury

Antimony

SECONDARY ASSESSMENT FILTER

Nitrite

39. The Nitrite accumulation time whilst significant is less than the self imposed 5 year period. Means of increasing this accumulation period need to be considered these include:

The natural oxidation of the nitrite to nitrate by natural Nitrobacter bacteria in the reservoir, assuming the reservoir is oxygenated at all parts then the activity of this process is likely to be significant. The formation of nitrate will not be a problem as this is precisely the mechanism considered in the Nitrate assessment that shows an accumulation period of 137 years.

As previously mentioned the actual releases from the site have been set so as to ensure a peak ground level concentration of NO_x substantially lower than the permitted maximum. The model has been re-run with this annual average concentration and accumulation time re-assessed. The results are shown in Table 6.

Fluoride

40. Fluoride is showing a short accumulation time because of the unrealistically high level of HF assumed using the short term air quality standard. Fluoride, compared to chlorine is a relatively rare contaminant in and throughout the process. There will be fluorine compounds in the engine fuel, but at very low levels, to go higher would lead to severe corrosion problems. As such it is proposed to take the predicted average HF concentration over the reservoir, from the ADMS model, and input this to the accumulation model. It is anticipated that this will increase the accumulation time but we need to reconsider and check the margin of safety before we can dismiss this issue.

Benzene

41. This infers that the air quality standard is not really respectful of the water quality standard. As with Fluorine the view is that the modelled benzene emission is dramatically greater than the predicted emissions from the proposed site. We intend

re running the accumulation model with Benzene releases closer to our predicted levels. Once again the margins of safety offered will dictate how we progress.

42. The site's potential benzene emissions will be very small. Benzene can be formed in the engine, usually by pyrolysing the engine oil in the gap between the top piston ring and the piston crown. Benzene is usually quoted as a proportion of the total hydrocarbon release, we propose keeping to this convention. The engine de NO_x system will almost inevitably include a pre oxidation catalyst which will further reduce any benzene. Once set up and operational the benzene can be measured to confirm or amend these predictions. Consistency with this measurement is normally guaranteed by maintaining the engine operating conditions and monitoring the lube oil consumption on the engine.

Mercury

43. It appears that the air quality standard does not respect the water quality standard. As with benzene the accumulation model used has modelled an unrealistically high concentration of mercury. Our exhausts will be substantially lower than these levels. Obviously no mercury is added to, or used in the process, so the only input remains contamination of the feed input. The main source of mercury is batteries, albeit the concentration has for a long time now been restricted. The Hirwaun process has been developed and tested so as not to be so aggressive as to break open batteries and so allow any mercury in the electrolyte to leach out. These batteries will be recovered in the Eddy current separator, where a periodic inspection will be used to ensure this "gentle" treatment is maintained and that batteries continue not to be significantly broken in the process. This is considered to be the best means of restricting the release of mercury.

44. Downstream of this separation stage come the thermal stages and in each of these there is extensive gas cleaning which will further reduce mercury passing into the engines.

45. Long term monitoring of mercury is to be investigated on two fronts, conventional stack monitoring and analysing the used engine lube oil. Mercury in this will indicate mercury in the fuel gas and may well give a better average release. Lube oil analysis is done in order to monitor engine wear.

Antimony

46. Antimony is a metal that finds a number of diverse uses, these include:

    - An alloying agent to increase the hardness of lead in products such as batteries and bearings.
    - A pigment in yellow paint.
    - A flame retardant, regularly used in textiles and other related uses.
    - Use in ceramic and glass manufacture

- A stabiliser for certain plastics

47. Few of these uses are likely to result in the antimony contaminating the fuel for any of the engines considered in this analysis.

48. It is believed that given the nature of the Enviroparks process a specific fuel will give a predictable level of antimony contamination. The main pyrolyser fuel considered at present is predicted to be very low in antimony.

49. Having considered the potential for contamination we assumed that only 1/9 of the total relevant heavy metals from the engine exhaust were indeed Antimony. Modelling of this showed little resulting impact from antimony. Clearly this underpinning assumption will be checked at commissioning of the plant.

50. If the fuel subsequently changes say to textile then the potential for antimony emissions needs to be reconsidered and checked. The current belief is that antimony will not present a problem.

51. As with mercury, analysis of used engine lube oil may act as an accurate surrogate means of assessing long term Antimony emission levels. Unlike mercury care will be needed in interpreting these results, for if the engines were to use white metal bearings or certain greases, then other sources of Antimony contamination of the lube oil exists other than that by the fuel. A check with the engine supplier has confirmed that there are no white metal bearings in the engines and that Antimony lubricant can be avoided.

Conclusions

52. This note has considered all the potential pollutants for which a water quality limit or objective exists from the proposed Hirwaun site.

53. Using ADMS to predict air concentrations and adapting existing data to quantify the transfer from air into water; The conclusion is that compliance with the air quality objectives ensures that the majority of releases are incapable of putting at risk the quality of the water either within or transferred from the Penderyn reservoir system.

54. Table 5 below lists the substances for which this statement is not correct. By modelling the releases anticipated from the plant, which are substantially less than that required for mere compliance with the air quality objective, each of these substances can be seen to present no substantive risk to the reservoir and its systems. Table 5 describes the monitoring systems and data to be used to monitor compliance with these normal operating conditions.

55. Enviroparks proposes that a direct communication be established with Welsh Water for any condition or release that if continued could lead to an exceedance of a water quality objective if it were to continue for a period of less than 5 years.

Table 5

Substances requiring monitoring for water quality impact and proposed monitoring methods

Substance	Direct monitoring	Indirect monitoring
Nitrite	On line plant continuous monitor	None, but plant will be driving to reduce total NOx emissions
Benzene	Bi annual stack analysis	Monitor engine lube oil consumption
Fluoride	On line plant continuous monitor for halogens	None (total halogen classification done bi annually)
Mercury	Bi annual stack analysis	Engine lube oil analysis
Antimony	Bi annual stack analysis	Engine lube oil analysis, and lubricant selection

56. By complying with the sites air quality objectives and the monitoring described in Table 5, the following accumulation times before harm can arise have been predicted and are shown in Table 6 below.

Table 6

Pollutant	Standard mg/lt	Conc rise in transfer mg/lt (Annual)	Conc rise/yr storage mg/lt	Years storage to exceed limit	Less than 5 yr standard?
Nitrate	50	2.04E-06	1.37E-02	137.76	No
Nitrite	0.5	2.21E-06	1.49E-02	33.55	No
Sulphate	250	3.00E-05	1.26E+00	198.05	No
Chloride	250	1.95E-05	2.05E+00	122.18	No
Fluoride	1.5	3.26E-09	2.89E-04	5194.68	No
Benzene	0.001	9.19E-10	3.79E-06	263.91	No
Cadmium	0.005	5.00E-09	2.06E-05	242.41	No
Mercury	0.001	1.83E-10	7.55E-07	1323.83	No
Lead	0.01	2.50E-07	1.03E-03	9.70	No
Arsenic	0.01	6.00E-09	2.48E-05	404.02	No
Antimony	0.005	2.03E-10	8.39E-07	5957.22	No
Chromium	0.05	1.00E-07	4.13E-04	121.21	No
Copper	2	1.00E-05	4.13E-02	48.48	No
Manganese	0.05	1.00E-06	4.13E-03	12.12	No
Nickel	0.02	2.00E-08	8.25E-05	242.41	No

57. It is proposed that once a year Enviroparks and Welsh Water formally meet to review Welsh Waters water quality data and other relevant data pertaining to the Penderyn Reservoir system and seek any correlation between the operation of the park and the quality of the reservoir. Should any correlation be found then the assumptions within this assessment should be reviewed.

Scoring system used for the Welsh Water Risk Assessment proforma:

1= It won’t happen

2= It could happen

3= It may happen

4= It will likely happen

5= It will happen

D S Ridley (Enertech) and A Owen (Envisage)

06/05/09